L5: Entry 3 of 19 File: PGPB Jul 11, 2002

DOCUMENT-IDENTIFIER: US 20020091169 A1
TITLE: Expanded porous thermoplastic polymer membranes and device for the production thereof

Summary of Invention Paragraph:
[0003] According to WO 92/17533, closed cell foamed films are produced from a foamable polymer and a supercritical fluid. Cell sizes of less than 1 .mu.m and cell densities between 10.sup.9 and 10.sup.15 cells/cm are stated to be achieved. According to this very complex method, the film is produced by way of an extruder with a slit nozzle, a supercritical fluid such as CO.sub.2 is introduced at room temperature to a pressure chamber through which the film is guided via rollers, nucleation takes place upon passage into a second chamber at standard pressure, and cell growth is achieved in the second chamber at a temperature >190.degree. C. by feeding the film between heat exchangers and optionally by tempering. Alternatively, the supercritical fluid can also be introduced directly into the polymer melt inside the extruder, prior to extrusion by the nozzle.

Summary of Invention Paragraph:
[0004] WO 89/00918 describes the manufacture of closed-cell microcellular foams from semicrystalline polymers such as polypropylene and polyethylene with cell sizes varying from 1 to 100 .mu.m. According to the method, the polymer, at elevated pressure and above its melting point, is saturated with gas, the polymer material is shaped by way of an extrusion nozzle or by injection-molding, the pressure is reduced for cell nucleation and foaming, and the temperature is then reduced to below the polymer's melting point in order to solidify the polymer foam. U.S. Pat. No. 4,473,665 discloses substantially the same method for the manufacture of closed-cell microcellular foams from amorphous polymers such as polystyrene, polyester, nylon, and polycarbonate, with cell sizes of approximately 2 to 25 .mu.m and a pore volume of 5 to 30%.

Summary of Invention Paragraph:
[0005] Such closed-cell polymer foams are, however, unsuitable for filtration membranes since, due to their closed-cell nature they exhibit virtually no, or at best a very low, flow rate or flux for a medium to be filtered, and possess insufficient pore volume. In addition, defects due to uncontrolled cell growth cannot be ruled out. A further disadvantage is that the closed-cells of such foams would need to be converted, in a further process, into an open-celled material in order to obtain usable membrane materials.

Summary of Invention Paragraph:
[0006] EP 0 754 488 A1 describes a method for producing open-celled microfiltration membranes from such closed-cell polymer foams, but the method carries with it the risk of membrane rupture. According to this method, the webs of material between the cells of the closed-cell polymer foams are broken by compressing and stretching the polymer foam at various temperatures. The flat membranes of polypropylene described therein, having a thickness of between 2 and 200 .mu.m, are said to have a wall thickness (B) to cell size (A) ratio of the polymer foam cells of less than 0.5, with a pore content not less than 50%.

Summary of Invention Paragraph:

[0007] WO 96/38221 discloses a method of making foamed polymer hollow fiber membranes. According to the method, a molten polymer is passed through an extrusion device, and the melt is charged with gas under pressure before entering a spinning nozzle which shapes the melt. The pressure drop upon emergence from the nozzle causes the polymer melt to foam, creating a porous hollow fiber membrane. The wall thickness of the hollow fiber is adjusted by stretching the hollow fiber membrane at an elevated temperature. The temperature of the melt in the extrusion device is regulated in such a way that for amorphous polymers it lies above the polymer's glass transition temperature, and for partially crystalline polymers it lies above the polymer's melting point. The size and shape of the pores are said to be adjustable by the extrusion parameters, such as pressure, temperature, extrusion screw shape and speed, as well as by the shape of the extrusion spinning nozzle. According to this method, foam structures having a pore size in the range from 10 to 20 .mu.m and cell densities of approximately 10.sup.10 cells/cm.sup.3, can be achieved. These are predominantly closed-cell foams with a randomly scattered proportion of open cells of between 5 and 40%. The disadvantages of this method are that the hollow-fiber membranes produced have inadequate pore volume and flux for technical applications, and defects due to uncontrolled cell growth are possible.

Summary of Invention Paragraph:
[0008] Accordingly, the objects of the present invention are to create defect-free foamed membranes made of thermoplastic polymers that have a large void fraction and a high proportion of open cells with a narrow pore size distribution, to provide a continuous method for manufacturing such membranes as well as an apparatus for carrying out the method. These objects and others which will become apparent to one of ordinary skill are summarized and described in detail below.

Detail Description Paragraph:
[0020] The pressure in the die, which may even be greater than that in the heat exchanger, depends on the flow resistance, and can be controlled via the flow velocity of the extrusion mass of the single phase polymer melt by its temperature and by the second melt pump preceding the die. The melt pumps before the inlet and outlet of the second mixing stage are preferably gear pumps. The pressure drop upon emergence from the die causes foaming of the polymer melt. The dies used to shape the membranes from the single phase melt are slit nozzles of the requisite membrane width for the manufacture of flat membranes, or hollow core nozzles for the manufacture of tubular membranes and hollow fiber membranes. In the case of the hollow core nozzles, a pressurized gas, for example compressed air, is advantageously used as the lumen-forming fluid.

Detail Description Paragraph:
[0021] Rather surprisingly it has been found that the foamed polymer membranes manufactured in accordance with the present invention exhibit a high proportion of open pores if the cell formers are substances that, under normal conditions, comprise at least two gases or at least two low-boiling-point liquids or a mixture of a gas and a low-boiling-point liquid wherein the gases or liquids or mixtures of gas and liquid have different diffusion rates with respect to the polymer melt. The cell formers should be inert with respect to the polymer(s) used in the extrusion mass. Carbon dioxide and water are most preferred as cell formers.

Detail Description Paragraph:
[0023] At processing temperatures above 100.degree. C. (temperature of the charged extrusion mass of the single phase polymer melt), water is preferably used as one of at least two components of the cell former and is utilized to produce the pores by opening the cells. When a mixture of inert gas and water is used as the cell former, as the polymer melt emerges from the die and as the pressure drop simultaneously occurs, the resulting boiling of the water brings about an additional cell pressure that is sufficient to burst the closed cells.

Detail Description Paragraph:

[0025] The cell formers can be introduced by way of a hollow needle through a sintered metal that preferably has pore sizes of approximately 20 .mu.m and smaller, in order to obtain the largest possible contact surface at the phase boundary between the polymer melt and the liquid and/or gas.

Detail Description Paragraph:
[0027] Membranes in the micro- and macrofiltration range, having average pore diameters between 0.05 .mu.m and 30 .mu.m and between 10 .mu.m and 200 .mu.m, respectively can be obtained. The membranes have a pore volume of at least 75%, a proportion of open cells of at least 80%, and a pore size distribution with a standard deviation of .+-.10% of the average pore diameter.

Detail Description Paragraph:
[0028] Void fraction or pore volume (as a percentage) is calculated using the formula (1-crude density/polymer density).times.100. Crude density is defined as the foam mass per unit volume, and was determined by weighing the mass and calculating the volume from the linear dimension of a suitable specimen. Proportion of open cells (as a percentage) was measured using an air displacement pycnometer. With this method, a geometric volume of a specimen is compared to a reference volume at identical pressure in order to ascertain the air displaced by the foamed material, i.e., the volume corresponding to the closed cells plus the foam mass. The error resulting from cut cells at the surface was corrected by way of measurements on specimens with various surface-to-volume ratios. The proportion of open cells was determined by extrapolating the measured proportion of open cells to a surface-to-volume ratio of zero. Pore size distribution was determined from the profile of the air flow rate plots as a function of pressure at the wetted membrane whose pores were filled with water. Air flow rates were measured with a Coulter porosimeter.

Detail Description Paragraph:
[0033] In this fashion, the temperature of the extrusion mass was reduced from an initial 260.degree. C. in the region of cylinder 4 located before gear pump 14 to approximately 150.degree. C. in heat exchanger 15 of the second mixing zone. The polymer melt was then shaped, using a wide-slit die 18 at a die temperature of 220.degree. C., into a flat film 40 cm wide, the polymer melt being foamed because of the pressure drop upon extrusion of the extrusion mass through the die.

Detail Description Paragraph:
[0034] The flat membrane manufactured in this fashion had a thickness of 0.4 mm, a cell or pore density of 10.sup.14 cells/cm.sup.3 and an average cell size of 0.5 .mu.m (.+-.0.03 .mu.m). Its void fraction or pore volume was 82%, 91% open cells. The water flux of the so-produced membrane was approximately 120 mL/(min/cm.sup.2/bar), while its bubble point was approximately 1.9 bar.

CLAIMS:

1. A foamed porous membrane of at least one thermoplastic polymer, wherein the membranes have a proportion of open cells of at least 80%, a void fraction of at least 75%, and an open-pore pore size distribution with a standard deviation of .+-.10% of the average pore diameter.

2. The membrane of claim 1 wherein said membrane has a pore diameter in the microfiltration range of from 0.05 .mu.m to 30 .mu.m.

3. The membrane of claim 1 wherein said membrane has a pore diameter in the macrofiltration range of from greater than 30 .mu.m to 200 .mu.m.

17. The apparatus of claim 12 wherein said die is configured as a wide-slit nozzle.

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Term:

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Search History

DATE: Friday, December 16, 2005 Printable Copy Create Case

Set Name side by side	Query	Hit Count	Set Name result set
DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD; PLUR=YES; OP=ADJ			
L8	axial direction same pore density	2	L8
L7	L2 and lengthwise same pore density	0	L7
L6	L2 and pore density same lengthwise	0	L6
L5	L2 and pore density	19	L5
L4	l2 and variable pore density	0	L4
L3	L2 and dense ends	0	L3
L2	hollow fiber membrane and pores and slit	231	L2
L1	membrane and hollow fiberor fibre and slit	0	L1

END OF SEARCH HISTORY

L14: Entry 1 of 1 File: USPT May 7, 1991

DOCUMENT-IDENTIFIER: US 5013439 A
TITLE: Microporous membranes having increased pore densities and process for making the same

Abstract Text (1):
Disclosed are a process for forming an open-celled microporous membrane (e.g., in film or fiber form) and a novel microporous membrane formed thereby. The process generally includes sequential cold and hot stretching operations, whereby the cold stretching operation is preferably accomplished in a plurality of discrete cold stretching steps. In this regard, the total cold stretch extension is of greater than about 30 percent, and advantageously greater than about 40 percent based upon the initial unstretched length of the nonporous precursor, with this total cold stretch ratio being distributed among a plurality of discrete cold stretching steps. The novel membranes of this invention are characterized by decreased pore size and increased pore densities. For example, the membranes of this invention will have an average pore radius as determined by mercury porosimetry of less than about 0.040 micron. The membranes of this invention, moreover, exhibit a distinctive "bluish" color hue (i.e., a Macbeth Coloreye.TM. b* value of less than about -10 as determined by placing a single ply sample of the membrane against a black background).

Brief Summary Text (2):
The present invention broadly relates to open-celled microporous membranes (e.g., in film or hollow fiber form) and to processes of making the same. The microporous membranes of the invention are characterized by increased pore densities and decreased pore sizes as compared to prior art microporous membranes of similar physical geometry. The membranes of the invention are prepared by sequential uniaxial cold and hot stretching (under conditions to be defined below) whereby the total cold stretch extension is significantly greater as compared to conventional membrane processing techniques, and is preferably accomplished in a series of discrete cold stretching steps.

Brief Summary Text (9):
Pore density is an important physical attribute of a microporous membrane since it directly determines the gas flux of the membrane (i.e., permeability). That is, the greater density of the pores in the microporous membrane, the greater the ability of the film to allow a volume of gas to flow through a fixed surface area of the membrane in a fixed period of time. Such permeabilities are usually expressed in terms of "Gurley Values" (sometimes also referred to as "Gurley Seconds"), which is the time required for 10 cm.sup.3 of air to pass through 1 in.sup.2 of membrane from one exterior surface to an opposite exterior surface thereof when a pressure differential of 12.2 inches of water is applied across the membrane. Since permeability is a measure of the ease of mass transfer across the membrane, lower Gurley Values correspond to lower mass transfer times and hence correspond to higher permeabilities and a concomitant greater ease of mass transfer.

Brief Summary Text (10):
The capability of membranes to have a greater ease of mass transfer thereacross is

important in many end use applications, such as filter media, solute extraction membranes, blood oxygenation membranes, battery separators, etcetera. However, since the pore density of microporous membranes (and its resulting permeability) is a function of pore size, in order to increase the pore density of a microporous membrane, the pore size must be correspondingly reduced. While the prior art processes noted above do permit microporous membranes to be produced which have satisfactory permeability properties, there still exists a continual need for improvements.

Brief Summary Text (11):
According to the present invention, novel open-celled microporous membranes are provided having increased pore densities and correspondingly reduced pore sizes as compared to conventional microporous membranes. Surprisingly, the novel membranes of the present invention are produced by subjecting a membrane precursor to an increased cold stretch which is preferably accomplished in multiple discrete uniaxial cold stretching steps prior to hot stretching. That is, the total amount of cold stretching of the membrane precursor is increased as compared to the cold stretching employed in conventional microporous membrane processes. And, this increased cold stretching is preferably distributed over multiple discrete cold stretching steps prior to hot stretching. Advantageously, the total cold stretch employed according to the present invention elongates the membrane precursor greater than about 30%, and more advantageously greater than about 40%, based upon its initial length prior to cold stretching, this total cold stretch preferably being distributed over two or more (preferably two to four) discrete sequential cold stretching steps.

Brief Summary Text (13):
The membranes of the present invention are open-celled and are particularly characterized by a reduced bulk density as compared to a corresponding membrane precursor having a nonopen-celled structure. Moreover, the membranes of this invention exhibit permeabilities (as determined by a gas flux of less than about 22 Gurley seconds), and an average pore density of greater than about 75 pores per square micron of membrane surface. The pores will typically have an average length as measured in the direction of the longitudinal stretching of less than about 0.10 micron (advantageously between about 0.05 to 0.09 micron), an average pore breadth as measured in a direction perpendicular to the longitudinal stretching of less than about 0.035 micron (advantageously between about 0.024 to 0.035 micron), an average pore surface area of less than about 2.5.times.10.sup.-3 square micron (advantageously between about 0.9.times.10.sup.-3 to 2.5.times.10.sup.-3 square micron), an average pore radius as determined by mercury porosimetry of less than about 0.040 micron (advantageously between about 0.0365 to 0.040 micron), and a specific surface area of greater than about 45 m.sup.2 /g (i.e., as determined by BET analysis using a Quantasorb.TM. apparatus manufactured by the Quantachrome Corporation--see also, S. Brunauer et al, Journal of American Chemical Society, vol. 60, pg. 309 (1938); and F. M. Nelson et al, Analytical Chemistry, vol. 30, pg. 1387 (1958), the entire content of each of these articles being expressly incorporated hereinto by reference, for a further discussion of BET analysis).

Brief Summary Text (14):
Moreover, the membranes of the present invention are translucent and exhibit a characteristic "bluish" color hue. Specifically, the membranes of this invention exhibit a b.sup.* value of less than -10, and more specifically between about -11 to about -14 when a single ply membrane sample is analyzed in a Macbeth Coloreye.TM. apparatus against a black background. The reasons for this "bluish" color hue are not fully understood at this time. However, without wishing to be bound to any particular theory, it is surmised that it is caused by the increased pore density and decreased pore size which apparently cause different diffusion and scattering of light in the visible spectrum as compared to conventional opaque membranes of similar geometry. This different scattering of light thus apparently translates into a visibly perceptible bluish color hue being imparted to the

membranes of this invention.

Detailed Description Text (21):
Surprisingly, it has been discovered that novel microporous membranes are formed having smaller pore sizes and increased pore densities when the total cold stretch extension imparted to the film is greater than 30%, and more advantageously greater than 40% as compared to the initial length of the precursor film. This cold stretching is moreover preferably accomplished in multiple discrete cold stretching steps. In this manner, the combined effect of increasing the total amount of extension imparted to the film during cold stretching, and preferably distributing this increased total cold stretching among a number of discrete cold stretching steps results in a membrane having lesser pore sizes and greater pore densities as compared to microporous membranes of the prior art which were not produced using the cold stretching technique of this invention.

Detailed Description Text (24):
FIG. 3 is a photomicrograph of a polypropylene microporous membrane according to this invention. As is seen, a very similar pore morphology is present as compared to the prior art membrane of FIG. 2. Significantly however, in order to obtain roughly comparable pore resolution in the photomicrograph, a magnification of 40,000.times. was required--i.e., twice the magnification of FIG. 2. This indicates qualitatively the decreased pore sizes and increased pore densities of the membranes of this invention as compared to similarly configured membranes of the prior art--i.e., as compared to membranes which were not produced using the cold stretching techniques of this invention.

Detailed Description Text (34):
As is apparent from the foregoing, Samples C and D according to this invention (i.e., since the total cold stretch being greater than 30%), exhibited pore sizes which are significantly less as compared to the pore sizes of comparative Sample E not in accordance with this invention (i.e., since the total cold stretch was less than 35%). Also, it will be noted that the specific surface area of Sample D according to this invention is significantly greater than the specific surface area of Comparative Example E indicating that the membranes of this invention also had increased pore densities.

Detailed Description Text (39):
The pore density of Samples C and D according to this invention were qualitatively determined and appear below in comparison to pore densities of a prior art Celgard.RTM. 2400 microporous polypropylene film.

Detailed Description Text (40):
The above data demonstrate that the membranes of this invention exhibit pore densities about twice that of a conventional microporous polypropylene membrane.

Detailed Description Paragraph Table (5):

	Pore Density (# of pores/square micron)
	Sample C 75 Sample D 105 Celgard .RTM. 2400
35-54	

Current US Original Classification (1):
210/500.23

CLAIMS:

1. A process for preparing an open-celled, microporous polymer membrane which comprises the steps of:

(a) uniaxially cold stretching a non-porous crystalline polymeric precursor to said membrane at a temperature in the range of between about -20.degree. C. to about

20.degree. C. below the crystalline melting point of the polymeric precursor, said uniaxial cold stretching being such that said polymeric precursor is extended greater than about 30% in length as compared to the initial length of said polymeric precursor; and

(b) uniaxially hot stretching in the same direction the cold stretched precursor achieved in the practice of step (a) at a temperature in the range of between about 20.degree. C. below the crystalline melting point of the polymeric precursor to about 5.degree. C. below the crystalline melting point of the polymeric precursor whereby to achieve a microporous polymer membrane having an open-celled structure consisting of a dense plurality of interconnected pores and characterized by having a reduced bulk density as compared to the bulk density of a corresponding nonopen-celled structure, and having a pore density of greater than about 75 pores per square micron of membrane surface area, and wherein the pores have an average length of less than about 0.10 micron, an average breadth of less than about 0.035 micron, and an average surface area of less than about 2.5.times.10.sup.-3 square micron.

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☐ 1. Document ID: US 5569198 A

Using default format because multiple data bases are involved.

L16: Entry 1 of 2 File: USPT Oct 29, 1996

US-PAT-NO: 5569198
DOCUMENT-IDENTIFIER: US 5569198 A

TITLE: Microporous catheter

DATE-ISSUED: October 29, 1996

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Racchini; Joel R.	Edina	MN		

US-CL-CURRENT: 604/103.01; 604/20, 604/21

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 2. Document ID: US 5013439 A

L16: Entry 2 of 2 File: USPT May 7, 1991

US-PAT-NO: 5013439
DOCUMENT-IDENTIFIER: US 5013439 A

TITLE: Microporous membranes having increased pore densities and process for making the same

DATE-ISSUED: May 7, 1991

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Fisher; Harold M.	Charlotte	NC		
Leone; Daniel E.	Charlotte	NC		
Lowery; James J.	Charlotte	NC		

US-CL-CURRENT: 210/500.23; 210/500.36, 264/156

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

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Terms	Documents
hollow fibers and membrane and pore density same ends	2

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L25: Entry 5 of 11 File: JPAB Nov 28, 1991

DOCUMENT-IDENTIFIER: JP 03267128 A
TITLE: POROUS HOLLOW FIBER

Abstract Text (1):
PURPOSE: To obtain the porous hollow fiber having high water permeability and fractionating property and with its flux not significantly reduced by forming the inner surface of the porous hollow fiber contg. a hydrophobic polymer and a hydrophilic polymer into a porous structure consisting of a dense layer having a minute slit and a reticular structure and providing a pore capable of permeating pure water at a specified rate to the outer surface.

Abstract Text (2):
CONSTITUTION: The porous hollow fiber contains 0.5-10% hydrophilic polymer (e.g. polyvinyl pyrrolidone) based on the hydrophobic polymer such as polysulfone, and is the porous structure consisting of the dense layer having minute slits at a rate of perforation of 10-50% and having 0-5.5μm thickness on the inner surface and the reticular structure integrated with the dense layer and continuously formed. The outer surface has pores having maximum diameter of 0.5-5μm formed by the partial opening of the reticular structure. The porous hollow fiber useful in separation is obtained by using the hollow fiber capable of permeating pure water at the rate of ≥1000l/m2.hr.kg.cm2.

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L25: Entry 8 of 11 File: JPAB Jul 8, 1983

DOCUMENT-IDENTIFIER: JP 58114702 A
TITLE: POLYSULFONE HOLLOW FIBER MEMBRANE AND ITS PRODUCTION

Abstract Text (1):
PURPOSE: To provide a titled hollow fiber membrane which allows permeation of substantially no materials larger tian 80Å and has ≥1.5m3/m3.hr.kg/cm2 rate of water permeation by specifying the width of the slit-like fine gaps on the inside surface and the sizes and opening rate of the micropores on the outside surface and providing fine porous structure to the inside of the membrane.

Abstract Text (2):
CONSTITUTION: This fibrous membrane has slit-like fine gaps of ≤500Å average width on the inside surface and has micropores of 1,000~5,000Å average pores sizes on the outside surface at ratios of 10~50% opening rate. The inside of the membrane has fine porous structure. Here, the slit-like fine gaps refer to the gaps existing in the longitudinal directions of the fibers and the average width is the average value of the short diameters thereof. The average pore size inversion D of the micropores is expressed by the equation (Di, Dn: the actually measured diameter of the i-th and n-th micropores, and with the pores which are not approximate to circular shapes, the diameter of the circles of the same areas as those of such pores). The hollow fibers are produced by adding polyethylene glycol of the amt. at which the soln. shows phase sepn. when the soln. is heated to 100°C to the soln. to prepare stock soln. for spinning. Said spinning soln. is subjected to dry and wet spinning, whereby said fibers are obtained.

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L25: Entry 8 of 11 File: JPAB Jul 8, 1983

DOCUMENT-IDENTIFIER: JP 58114702 A
TITLE: POLYSULFONE HOLLOW FIBER MEMBRANE AND ITS PRODUCTION

Abstract Text (1):
PURPOSE: To provide a titled hollow fiber membrane which allows permeation of substantially no materials larger tian 80Å and has ≥1.5m3/m3.hr.kg/cm2 rate of water permeation by specifying the width of the slit-like fine gaps on the inside surface and the sizes and opening rate of the micropores on the outside surface and providing fine porous structure to the inside of the membrane.

Abstract Text (2):
CONSTITUTION: This fibrous membrane has slit-like fine gaps of ≤500Å average width on the inside surface and has micropores of 1,000~5,000Å average pores sizes on the outside surface at ratios of 10~50% opening rate. The inside of the membrane has fine porous structure. Here, the slit-like fine gaps refer to the gaps existing in the longitudinal directions of the fibers and the average width is the average value of the short diameters thereof. The average pore size inversion D of the micropores is expressed by the equation (Di, Dn: the actually measured diameter of the i-th and n-th micropores, and with the pores which are not approximate to circular shapes, the diameter of the circles of the same areas as those of such pores). The hollow fibers are produced by adding polyethylene glycol of the amt. at which the soln. shows phase sepn. when the soln. is heated to 100°C to the soln. to prepare stock soln. for spinning. Said spinning soln. is subjected to dry and wet spinning, whereby said fibers are obtained.

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☐ 1. Document ID: JP 2005111456 A

L25: Entry 1 of 11 File: JPAB Apr 28, 2005

PUB-NO: JP02005111456A
DOCUMENT-IDENTIFIER: JP 2005111456 A
TITLE: FILTER OF POLLUTANT WATER AND THE LIKE, USING FILM TYPE FILTRATION-MEMBRANE MATERIAL, STRAINEDLY AND PARALLELED LAMINATED MANY SUPERFINE FILAMENTS

PUBN-DATE: April 28, 2005

INVENTOR-INFORMATION:

NAME	COUNTRY
MORIMURA, TADAKI	

INT-CL (IPC): B01 D 33/06; B01 D 39/16

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 2. Document ID: JP 09308685 A

L25: Entry 2 of 11 File: JPAB Dec 2, 1997

PUB-NO: JP409308685A
DOCUMENT-IDENTIFIER: JP 09308685 A
TITLE: HOLLOW FIBER MEMBRANE FOR BLOOD PURIFICATION AND BLOOD PURIFYING DEVICE

PUBN-DATE: December 2, 1997

INVENTOR-INFORMATION:

NAME	COUNTRY
NAGAMATSU, HIROSHI	
TAKADA, SATORU	

INT-CL (IPC): A61 M 1/18; A61 M 1/18; B01 D 69/08; B01 D 71/68

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 3. Document ID: JP 05209313 A

L25: Entry 3 of 11 File: JPAB Aug 20, 1993

PUB-NO: JP405209313A
DOCUMENT-IDENTIFIER: JP 05209313 A
TITLE: HOLLOW FIBER

PUBN-DATE: August 20, 1993

INVENTOR-INFORMATION:
NAME COUNTRY
STOPPONI, ALESSANDRO
DEMOFONTI, CLAUDIO
VALENTINI, CLAUDIO
SISTO, RAFFAELLO
PEDRETTI, UGO

INT-CL (IPC): D01F 6/78; B01D 71/52; D01D 5/24; D01F 6/00

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 4. Document ID: JP 04197487 A

L25: Entry 4 of 11 File: JPAB Jul 17, 1992

PUB-NO: JP404197487A
DOCUMENT-IDENTIFIER: JP 04197487 A
TITLE: APPARATUS FOR TREATING WASTE WATER

PUBN-DATE: July 17, 1992

INVENTOR-INFORMATION:
NAME COUNTRY
YAMAMOTO, NOBORU
NISHITOI, MUTSUMI

US-CL-CURRENT: 210/220
INT-CL (IPC): C02F 1/44; B01D 61/14; B01D 63/02; B01D 65/02; C02F 3/12

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 5. Document ID: JP 03267128 A

L25: Entry 5 of 11 File: JPAB Nov 28, 1991

PUB-NO: JP403267128A
DOCUMENT-IDENTIFIER: JP 03267128 A
TITLE: POROUS HOLLOW FIBER

PUBN-DATE: November 28, 1991

INVENTOR-INFORMATION:

NAME	COUNTRY
KOMATSU, KENSAKU	
OKAMOTO, TAKEHIKO	
KUSUDO, OSAMU	

US-CL-CURRENT: 210/500.23
INT-CL (IPC): B01D 69/08; B01D 69/02; D01D 5/24; D01F 6/00; D01F 6/76; B01D 71/68

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 6. Document ID: JP 59204911 A

L25: Entry 6 of 11 File: JPAB Nov 20, 1984

PUB-NO: JP359204911A
DOCUMENT-IDENTIFIER: JP 59204911 A
TITLE: REGENERATED CELLULOSE HOLLOW FIBER OF NOVEL STRUCTURE

PUBN-DATE: November 20, 1984

INVENTOR-INFORMATION:

NAME	COUNTRY
IWATA, MICHITAKA	
MANABE, SEIICHI	
INOUE, MAMORU	

INT-CL (IPC): D01F 2/00; B01D 13/00; D01F 2/04

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

☐ 7. Document ID: JP 58115115 A

L25: Entry 7 of 11 File: JPAB Jul 8, 1983

PUB-NO: JP358115115A
DOCUMENT-IDENTIFIER: JP 58115115 A
TITLE: PREPARATION OF REGENERATED CELLULOSIC HOLLOW FIBER

PUBN-DATE: July 8, 1983

INVENTOR-INFORMATION:

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INT-CL (IPC): D01F 2/28; D06M 1/20

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

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L25: Entry 8 of 11 File: JPAB Jul 8, 1983

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DOCUMENT-IDENTIFIER: JP 58114702 A
TITLE: POLYSULFONE HOLLOW FIBER MEMBRANE AND ITS PRODUCTION

PUBN-DATE: July 8, 1983

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INT-CL (IPC): B01D 13/00; D01F 6/96

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

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DOCUMENT-IDENTIFIER: JP 57066114 A
TITLE: POROUS POLYETHYLENE HOLLOW FIBER AND ITS PRODUCTION

PUBN-DATE: April 22, 1982

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INT-CL (IPC): D01F 6/04

Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw D

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L25: Entry 10 of 11 File: JPAB Aug 18, 1980

PUB-NO: JP355107505A
DOCUMENT-IDENTIFIER: JP 55107505 A
TITLE: PRODUCTION OF HOLLOW FIBER

PUBN-DATE: August 18, 1980

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INT-CL (IPC): D01F 2/28

Refine Search

Search Results -

Terms	Documents
areas same reduced porosity and hollow fiber and membrane	2

Database:
US Pre-Grant Publication Full-Text Database
US Patents Full-Text Database
US OCR Full-Text Database
EPO Abstracts Database
JPO Abstracts Database
Derwent World Patents Index
IBM Technical Disclosure Bulletins

Search: L35

Refine Search | Recall Text | Clear | Interrupt

Search History

DATE: Friday, December 16, 2005 Printable Copy Create Case

Set Name side by side	Query	Hit Count	Set Name result set
DB=USPT; PLUR=YES; OP=ADJ			
L35	areas same reduced porosity and hollow fiber and membrane	2	L35
L34	hollow fibers and areas same reduced density	3	L34
L33	reducing pore density and hollow fibers same ends	0	L33
L32	hollow fiber ends same reduced density	0	L32
L31	L30 and pore size same density	0	L31
L30	L29 and fibers section	2	L30
L29	stretching and hollow fibers and membrane and cold and hot	118	L29
DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD; PLUR=YES; OP=ADJ			
L28	hollow fiber and cold and hot same streach?	0	L28
DB=JPAB; PLUR=YES; OP=ADJ			
L27	L25 and pore size and length	0	L27
L26	L25 and pore density	0	L26
L25	hollow fibers and pores and slit	11	L25
L24	L23 and pore density	0	L24

L23	hollow fiber and stretch	6	L23
L22	hollow fiber and cold stretch and hot stretch	0	L22
L21	pore density and hollow fiber	1	L21
L20	reducing pore density and hollow fibre	0	L20
L19	axial direction same pore density	0	L19
L18	hollow fiber ends same pore density	0	L18
L17	hollow fibers and membrane and pore density same ends	0	L17
DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD; PLUR=YES; OP=ADJ			
L16	hollow fibers and membrane and pore density same ends	2	L16
L15	210/500.23.ccls. and pore density	28	L15
L14	L13 and reduced pore size	1	L14
L13	210/500.23.ccls. and pore density	28	L13
L12	hollow fiber ends same pore density	0	L12
L11	hollow fiber ends same pore debsity	0	L11
L10	hollow fiber same variable pore density	0	L10
L9	pore density same potted area and amembrane	0	L9
L8	axial direction same pore density	2	L8
L7	L2 and lengthwise same pore density	0	L7
L6	L2 and pore density same lengthwise	0	L6
L5	L2 and pore density	19	L5
L4	l2 and variable pore density	0	L4
L3	L2 and dense ends	0	L3
L2	hollow fiber membrane and pores and slit	231	L2
L1	membrane and hollow fiberor fibre and slit	0	L1

END OF SEARCH HISTORY

L5: Entry 9 of 19 File: USPT Feb 6, 1996

DOCUMENT-IDENTIFIER: US 5489382 A
** See image for Certificate of Correction **
TITLE: Oxygenator using porous hollow fiber membrane

Abstract Text (1):
The present invention is directed to an oxygenator using a hydrophobic porous hollow fiber membrane possessing an inside diameter in the range of 150 to 300 microns, a wall thickness in the range of 10 to 150 microns, and a substantially circular cross section, which porous hollow fiber membrane possesses an average crimp amplitude in the range of 35 to 120% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, and a crimp ratio in the range of 1.0 to 3.0%, and a method for the production thereof.

Brief Summary Text (3):
This invention relates to a porous hollow fiber membrane, a method for the production thereof, and an oxygenator using the hollow fiber membrane. More particularly, this invention relates to a porous hollow fiber membrane possessing a high gas-exchange capacity and, at the same time, offering a large available membrane area for the exchange of gas, a method for the production thereof, and an oxygenator using the hollow fiber membrane. Still more particularly, this invention relates to a porous hollow fiber membrane which, no matter whether the oxygenator to be used may be adapted to pass blood inside or outside the hollow fiber membrane, refrains from inflicting damage to the blood cell components or aggravating pressure loss, exhibits high efficiency in establishing gas-liquid contact, suffers from no blood plasma leakage over a protracted service, and manifests a high gas-exchange capacity, a method for the production thereof, and an oxygenator using the hollow fiber membrane.

Brief Summary Text (5):
Generally in the surgical operation of the heart, for example, an oxygenator of hollow fiber membrane is used in the extracorporeal circulation system for the purpose of leading a patient's blood out of his body and adding oxygen to and removing carbon dioxide gas from the blood. The hollow fiber membranes available for the oxygenator of this nature fall under two kinds; homogenous membranes and porous membranes. The homogeneous membranes attain movement of a gas by the molecules of the permeating gas being dissolved and dispersed in the membrane. These homogeneous membranes are represented by silicone rubber (commercialized by Senkouika Kogyo under trademark designation of "Mella-Silox," for example). In the homogeneous membranes, the silicone rubber membrane is the only product that has been heretofore accepted as practicable from the standpoint of gas permeability. The silicone rubber membrane is not allowed to have any smaller wall thickness than 100 .mu.m on account of limited strength. Thus, it has a limited capacity for permeation of gas and it is particularly deficient in the permeation of carbon dioxide gas. Moreover, the silicone rubber has a disadvantage in that it is expensive and low in fabricability.

Brief Summary Text (6):
By contrast, in the porous membranes, since the micropores possessed by the membrane are notably large as compared with the molecules of a gas to be permeated,

the gas passes through the micropores in the form of volume flow. Various oxygenators using a microporous polypropylene membrane have been proposed. It has been proposed, for example, to produce porous polypropylene hollow fibers by melt spinning polypropylene through hollow fiber producing nozzles at a spinning temperature in the range of 210.degree. to 270.degree. C. at a draft ratio in the range of 180 to 600, then subjecting the resultant hollow threads of polypropylene to a first heat treatment at a temperature not exceeding 155.degree. C., stretching the heated hollow threads by a ratio in the range of 30 to 200% at a temperature not exceeding 110.degree. C., and thereafter subjecting the stretched hollow threads to a second heat treatment at a temperature exceeding that of the first heat treatment and not exceeding 155.degree. C. (Japanese Patent Publication SHO 56 (1981)-52,123). These porous hollow fibers obtained by the method just mentioned are physically caused to form micropores therein by the hollow threads of polypropylene being stretched. These micropores, therefore, are linear micropores extending substantially perpendicularly horizontally relative to the wall thickness proportionately to the degree of stretching while forming cracks in the axial direction of the hollow fiber. Thus, they have a cross section of the shape of a slit. Further, the micropores run substantially linearly and continuously through the wall thickness and occur in a high void ratio. The porous hollow fibers, therefore, have a disadvantage in that they have high permeability to steam and, after a protracted use for extracorporeal circulation of blood, they suffer from leakage of blood plasma.

Brief Summary Text (7):
As a porous membrane incapable of blood plasma leakage, for example, there has been proposed a porous polyolefin hollow fiber membrane which is produced by mixing a polyolefin, an organic filler uniformly dispersible in the polyolefin in the molten state thereof and easily soluble in a liquid extractant to be used, and a crystal seed forming agent, melting the resultant mixture, discharging the molten mixture through annular spinning nozzles and, at the same time, introducing an inert gas into the inner cavities of the spun tubes of the molten mixture, causing the resultant hollow threads to contact a cooling and solidifying liquid incapable of dissolving the polyolefin thereby cooling and solidifing the hollow threads, then bringing the cooled and solidified hollow threads into contact with a liquid extractant incapable of dissolving the polyolefin thereby extracting the organic filler from the hollow threads (Japanese Patent Application SHO 59(1984)-210,466). The polypropylene hollow fiber membrane which, as one species of the hollow fiber membranes, is produced by using as a cooling and solidifying liquid a specific cooling and solidifying liquid heretofore favorably utilized on account of the ability thereof to dissolve the organic filler does not suffer from blood plasma leakage because the pores formed therein are small in diameter and complicated in pattern of channel. Since this membrane has a small pore density per unit area, it has a possibility of exhibiting a gas-exchange capacity insufficient for the membrane to be used effectively in an oxygenator. It also has another possibility that the low molecular component of the polyolefin will mingle into the cooling and solidifying liquid capable of dissolving the organic filler and eventually adhere to the inner wall of the cooling bath tube and cause deformation of the shape of hollow fiber with elapse of time.

Brief Summary Text (8):
To overcome the impact of such a drawback as mentioned above, there has been proposed a porous polyolefin hollow fiber membrane which is produced by mixing polypropylene, an organic filler uniformly dispersible in the polypropylene in the molten state thereof and readily soluble in a liquid extractant to be used, and a crystal seed forming agent, melting the resultant mixture and discharging the molten mixture through annular spinning nozzles into hollow threads, allowing the hollow threads to contact a liquid made of the organic filler or a similar compound thereby cooling and solidifying the hollow threads, then bringing the cooled and solidified hollow threads into contact with a liquid extractant incapable of melting the propylene thereby extracting the organic filler from the hollow threads

(Japanese Patent Application SHO 61(1986)-155,159). The hollow fiber membrane produced by this method is free from the drawbacks described so far. During the course of the cooling, however, the organic filler or the cooling and solidifying liquid remains locally on the outermost surface of hollow fibers before these hollow fibers are thoroughly cooled and solidified and the compositional proportion of polypropylene is lower in the outermost surface than elsewhere in the entire wall thickness and, as a result, the pores in the outer surface of hollow fiber are large and the propylene particles are interconnected in the pattern of a network and distributed in a heavily rising and falling state. The hollow fibers of this nature pose no problem whatever when they are used in an oxygenator of the type adapted to effect addition of oxygen to blood and removal of carbon dioxide gas therefrom by flowing the blood inside the hollow fibers and blowing an oxygen-containing gas outside the hollow tubes.

Brief Summary Text (9):
When the hollow fibers are used in an oxygenator of the type adapted to effect the same functions by flowing blood outside the hollow fibers and blowing the oxygen-containing gas inside the hollow fibers, however, they have a disadvantage that the aforementioned behavior of the outer surface inflict damage to the blood cell components and aggravate the pressure loss. The hollow fiber membrane, without reference to the type of oxygenator, has a disadvantage that the work of assembling the hollow fibers into the oxygenator neither proceeds efficiently nor produces a desirable potting because the adjacent hollow fibers coalesce.

Brief Summary Text (10):
In the case of the oxygenator which is formed of the porous hollow fiber membranes obtained as described above and is operated by circulating blood outside the hollow fiber membranes and blowing an oxygen-containing gas inside the hollow fiber membranes, if the gaps between the adjacent hollow fibers are narrow and substantially uniform in width throughout the entire length of hollow fibers, the air or the oxygen-containing gas is liable to stagnate easily in these gaps because of the hydrophobicity of the hollow fiber membranes. If the stagnation of the air or the oxygen-containing gas or the so-called phenomenon of air trap arises in the gaps between the adjacent hollow fibers, it impairs the flow of blood and entails a disadvantage that the clusters of the entrapped air or oxygen-containing gas obstruct the blood from gaining access to the air or oxygen-containing gas through the hollow fiber membranes, lend themselves to descreasing the available membrane area, and degrade the oxygenator's gas-exchange capacity.

Brief Summary Text (11):
An object of this invention, therefore, is to provide an improved porous hollow fiber membrane, a method for the production thereof, and an oxygenator using the hollow fiber membrane. Another object of this invention is to provide a porous hollow fiber membrane possessing a high gas-exchange capacity and, at the same time, offering a large available membrane area for exchange of gas, a method for the production thereof, and an oxygenator using the hollow fiber membrane. A further object of this invention is to provide a porous hollow fiber membrane of polypropylene which, without reference to the type of oxygenator, refrains from inflicting damage to the blood cell components and aggravating the pressure loss, entails no blood plasma leakage over a protracted service, experiences no decline of the gas-exchange capacity due to the air trap, exhibits a high gas-exchange capacity, and warrants-favorable use in an oxygenator using the hollow fiber membrane. Yet another object of this invention is to provide a porous hollow fiber membrane possessing a smooth outer surface and defying coalescence of the adjacent hollow fibers during the assembly of an oxygenator, a method for the production thereof, and an oxygenator using the hollow fiber membrane.

Brief Summary Text (13):
The objects mentioned above are accomplished by a hydrophobic porous hollow fiber membrane possessing an inside diameter in the range of 150 to 300 microns, a wall

thickness in the range of 10 to 150 microns, and a substantially circular cross section, which porous hollow fiber membrane possesses an average crimp amplitude in the range of 35 to 120% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, and a crimp ratio in the range-of 1.0 to 3.0%.

Brief Summary Text (14):
This invention also discloses a porous hollow fiber membrane wherein the void ratio is in the range of 5 to 60%. This invention further discloses a porous hollow fiber membrane wherein the oxygen gas flux is in the range of 0.1 to 2,000 l/min.m.sup.2.atm. This invention discloses a porous hollow fiber membrane wherein the inside diameter is in the range of 180 to 250 .mu.m and the wall thickness is in the range of 20 to 100 .mu.m. This invention also discloses a porous hollow fiber membrane which is made of polypropylene. This invention further discloses a porous hollow fiber membrane wherein the average crimp amplitude is in the range of 50 to 100% of the outside diameter, the maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio is in the range of 0.02 to 0.05, and the crimp ratio is in the range of 2.0 to 3.0%.

Brief Summary Text (15):
This invention discloses a hydrophobic porous hollow fiber membrane which is a porous hollow fiber membrane of a polyolefin. This invention also discloses a porous hollow fiber membrane wherein minute polyolefin particles are intimately are bound and allowed to form a tightly packed layer on the inner surface side of the hollow fiber membrane, minute polyolefin particles are bound after the pattern of chains and allowed to form a porous layer on the outer surface side of the hollow fiber membrane, and very small through holes are formed in the hollow fiber membrane as extended from the inner surface side to the outer surface side.

Brief Summary Text (16):
This invention further discloses a porous hollow fiber membrane wherein the average crimp amplitude is in the range of 50 to 100% of the outside diameter, the maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio is in the range of 0.02 to 0.05, and the crimp ratio is in the range of 2.0 to 3.0%.

Brief Summary Text (17):
This invention discloses a porous hollow fiber membrane wherein the solid phase in the inner surface of the hollow fiber membrane has polypropylene particles partly exposed through the surface and preponderantly fused and bound intimately to give rise to a continuous phase, the solid layer in the interior through the outer surface of the membrane has polypropylene particles arranged in the axial direction of fiber to give rise to a multiplicity of polypropylene clusters, and the gaps between the solid phases are interconnected in the form of a three-dimensional network to give rise to through holes.

Brief Summary Text (18):
This invention also discloses a porous hollow fiber membrane wherein the polypropylene particles have an average particle diameter in the range of 0.1 to 2.0 microns and an average pore diameter in the inner surface in the range of 0.1 to 1.0 micron. This invention further discloses a porous hollow fiber membrane which, when used in an oxygenator, is substantially free from leakage of blood plasma and decline of gas-exchange capacity within 30 hours of service.

Brief Summary Text (19):
This invention discloses a porous hollow fiber membrane which, when used in an oxygenator, inflicts damage sparingly on blood cell components. This invention discloses a porous hollow fiber membrane wherein the average crimp amplitude is in the range of 50 to 100% of the outside diameter, the maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude is in the range of 0.02 to 0.05, and the crimp ratio is in the range of 2.0 to 3.0%.

Brief Summary Text (20):
The objects mentioned above are also accomplished by a method for the production of a porous hollow fiber membrane, which is characterized by mixing a polyolefin, an organic filler uniformly dispersible in the polyolefin in the molten state thereof and easily soluble in a liquid extractant to be used, and a crystal seed forming agent, melting the resultant mixture and discharging the molten mixture through annular spinning nozzles into hollow threads, allowing the hollow threads to contact a cooling and solidifying liquid incapable of dissolving the polyolefin thereby cooling and solidifying the hollow threads, then bringing the resultant cooled and solidified hollow threads into contact with the liquid extractant incapable of dissolving the polyolefin thereby extracting the organic filler from the hollow threads, and thermally crimping the hollow threads thereby forming porous hollow fiber membranes possessing an average crimp amplitude in the range of 35 to 120% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, and a crimp ratio in the range of 1.0 to 3.0%.

Brief Summary Text (21):
This invention discloses a method for the production of a porous hollow fiber membrane wherein the crimp is formed by causing the produced hollow fiber membrane to be cross wound on a bobbin and then heat set. This invention also discloses a method for the production of a porous hollow fiber membrane wherein the heat setting is carried out at a temperature in the range of 50.degree. to 100.degree. C. for a period in the range of 2 to 48 hours. This invention further discloses a method for the production of a porous hollow fiber membrane wherein the polyolefin is polypropylene. This invention discloses a method for the production of a porous hollow fiber membrane wherein the organic filler is a hydrocarbon having a boiling point exceeding the melting point of the polyolefin. This invention also discloses a method for the production of a porous hollow fiber membrane wherein the hydrocarbon is liquid paraffin or an .alpha.-olefin oligomer.

Brief Summary Text (22):
This invention further discloses a method for the production of a porous hollow fiber membrane wherein the amount of the organic filler to be incorporated therein is in the range of 35 to 170 parts by weight, based on 100 parts by weight of the polyolefin. This invention discloses a method for the production of a porous hollow fiber membrane wherein the crystal seed forming agent is an organic heat-resistant substance possessing a melting point exceeding 150.degree. C. and a gelling point exceeding the crystallization initiating point of the polyolefin to be used. This invention also discloses a method for the production of a porous hollow fiber membrane wherein the amount of the crystal seed forming agent to be incorporated therein is in the range of 0.1 to 5 parts by weight, based on 100 parts by weight of the polyolefin.

Brief Summary Text (23):
This invention further discloses a method for the production of a porous hollow fiber membrane wherein the cooling and solidifying liquid possesses a specific heat capacity in the range of 0.3 to 0.7 cal/g. This invention discloses a method for the production of a porous hollow fiber membrane wherein the cooling and solidifying liquid is silicone oil or polyethylene glycol. This invention also discloses a method for the production of a porous hollow fiber membrane wherein the polydimethyl siloxane possesses a viscosity in the range of 2 to 50 cSt at 20.degree. C. This invention further discloses a method for the production of a porous hollow fiber membrane wherein the polyethylene glycol possesses an average molecular weight in the range of 100 to 400.

Brief Summary Text (24):
This invention discloses a method for the production of a porous hollow fiber membrane wherein the organic filler is liquid paraffin. This invention also

discloses a method for the production of a porous hollow fiber membrane wherein the amount of the organic filler to be incorporated therein is in the range of 35 to 170 parts by weight, based on 100 parts by weight of polypropylene.

Brief Summary Text (25):
This invention further discloses a method for the production of a porous hollow fiber membrane wherein the crystal seed forming agent is an organic heat-resistant substance possessing a melting point exceeding 150.degree. and a gelling point exceeding the crystallization initiating point of the polypropylene to be used. This invention discloses a method for the production of a porous hollow fiber membrane wherein the amount of the crystal seed forming agent to be incorporated therein is in the range of 0.1 to 5 parts by weight, based on 100 parts by weight of the polypropylene to be used.

Brief Summary Text (26):
The objects mentioned above are further accomplished by an oxygenator provided with hollow fiber membranes as gas-exchange membranes, which oxygenator is characterized by using hydrophobic porous hollow fiber membranes as gas-exchange membrane.

Drawing Description Text (2):
FIG. 1 is a schematic cross section of an apparatus to be used in the method for the production of porous hollow fiber membrane contemplated by the present invention,

Drawing Description Text (3):
FIG. 2 is a half cross section illustrating a typical hollow-fiber membrane type oxygenator as one embodiment of the present invention,

Drawing Description Text (4):
FIG. 3 is a cross section illustrating different portions of the embodiment of FIG. 2 relative to the packing ratio of hollow fiber membranes,

Drawing Description Text (5):
FIG. 4 is a half cross section illustrating another typical hollow-fiber membrane type oxygenator as another embodiment of this invention, and

Detailed Description Text (2):
The porous hollow fiber membrane of the present invention is a hydrophobic porous hollow fiber membrane possessing an inside diameter in the range of 150 to 300 microns, preferably 180 to 250 microns, a wall thickness in the range of 10 to 150 microns, preferably 20 to 100 microns, and a substantially circular cross section, which porous hollow fiber membrane is characterized by possessing an average crimp amplitude in the range of 35 to 120%, preferably 50 to 100%, of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, preferably 0.02 to 0.05, and a crimp ratio in the range of 1.0 to 3.0%, preferably 2.0 to 3.0%.

Detailed Description Text (3):
In the porous hollow fiber membrane of this invention, the average crimp amplitude is defined by the range of 35 to 120% of the outside diameter for the following reason. If the average crimp amplitude is less than 35% of the outside diameter, there arises the possibility that when porous hollow fiber membranes are incorporated in an oxygenator, the gaps allowed to intervene between the adjacent hollow fibers are not amply large and are liable to entail ready stagnation of air or an oxygen-containing gas therein. Conversely, if the average crimp amplitude exceeds 120% of the outside diameter, the disadvantage ensues that the gaps allowed to intervene between the individual hollow fibers during the incorporation of the porous hollow fiber membrane into the oxygenator cannot be easily retained in a size falling within a prescribed range.

Detailed Description Text (4):
The maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio is defined by the range of 0.01 to 0.1 for the following reason. If the maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio is less than 0.01, there similarly arises the possibility that when porous hollow fiber membranes are incorporated in an oxygenator, the gaps allowed to intervene between the adjacent hollow fibers are not amply large and are liable to entail ready stagnation of air or an oxygen-containing gas therein. Conversely, if the maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio exceeds 0.1, the disadvantage ensues that the gaps allowed to intervene between the individual hollow fibers during the incorporation of the porous hollow fiber membranes into the oxygenator are susceptible to larger variation in size than is tolerable and the flow of blood passed through the gaps suffers from heavy pressure loss.

Detailed Description Text (5):
The crimp ratio is also defined by the range of 1.0 to 3.0% for the following reason. If the crimp ratio is less than 1.0%, the gaps allowed to intervene between the individual hollow fibers during the incorporation of the porous hollow fiber membranes into the oxygenator are not fully effectively augmented by crimping. Conversely, if the crimp ratio exceeds 3.0%, the possibility ensues that the oxygenator produced as a module by the use of the porous hollow fiber membranes assumes a larger size than is tolerable.

Detailed Description Text (6):
So long as the porous hollow fiber membrane of this invention possesses the attributes described above, the methods for manufacture, specifically for crimping and for impartation of porosity are irrelevant. Such a porous hollow fiber membrane as satisfying the requirement may be obtained, for example, by preparing a hollow fiber membrane spun out and vested with a porous texture by the stretching method or the extraction method, cross winding it on a suitable bobbin, and heat treating the resultant roll of hollow fiber membrane approximately under the conditions of 60.degree. C. and 18 hours thereby setting the hollow fiber membrane in the crimped state. If the thermal setting aimed at the impartation of crimp is performed more than is necessary and the texture of membrane is consequently altered and specifically the void ratio existing before the crimping is lowered in a ratio of more than 60% under the impact of the heat treatment, then the thermal setting fails to manifest the effect thereof sufficiently. If the thermal setting is insufficient and the hollow fiber membrane which retains the crimped state desirably during the course of module assembly is consequently suffered to lose crimp under the tension subsequently exerted thereon by the residual stress, then the thermal setting does not manifest the effect thereof as expected.

Detailed Description Text (7):
The porous hollow fiber membrane of the present invention can be expected, when it is used in an oxygenator, to manifest the effect thereof more advantageously when it possesses a void ratio in the range of 5 to 60% and an oxygen gas flux in the range of 0.1 to 2,000 l/min.m.sup.2.atm., preferably 100 to 1,500 l/min.m.sup.2.atm. If the void ratio is less than 10%, there arises the possibility that the porous hollow fiber membrane is deficient in gas-exchange capacity. Conversely, if the void ratio exceeds 60%, the porous hollow fiber membrane has the possibility of entailing leakage of blood plasma.

Detailed Description Text (8):
If the opening ratio is less than 10%, there is the possibility that the formation of through holes in the void parts of the hollow fiber membrane does not take place sufficiently and the porous hollow fiber membrane betray deficiency in gas-exchange capacity. Conversely, if the opening ratio exceeds 30%, the through holes are deprived of necessary complexity of pattern and the porous hollow fiber membrane is susceptible of blood plasma leakage.

Detailed Description Text (9):
If the oxygen gas flux deviates from the range of 100 to 1,500 lit/min.m.sup.2.atm, there arises the possibility that the porous hollow fiber membrane fails to fulfil the function as a gas-exchange membrane. The polypropylene particles and the through holes or the gaps between the particles with jointly constitute the porous hollow fiber membrane of the present invention can be regulated in size and degree of distribution under desirable conditions.

Detailed Description Text (10):
The average particle diameter of the polypropylene particles is desired to be in the range of 0.1 to 2.0 .mu.m, preferably 0.2 to 1.5 .mu.m, and the average diameter of the pores in the inner surface is desired to be in the range of 0.1 to 1.0 .mu.m, preferably 0.3 to 0.6 .mu.m.

Detailed Description Text (11):
The materials available for the construction of the porous hollow fiber membrane of the present invention include hydrophobic synthetic -resins represented by such, polyolefins as polypropylene and polyethylene and polytetrafluoroethylene, for example. Among other hydrophobic synthetic resins mentioned above, polypropylene is particularly advantageous in excelling in various properties such as mechanical strength, thermal stability, and fabricability and permitting easy impartation of porosity.

Detailed Description Text (12):
The cross-sectional configuration of the hollow fiber membrane is variable in some measure with the production conditions used for the hollow fiber membrane. Generally, very small polyolefin particles are closely bound to form a tightly packed layer on the inner surface side and similarly small polyolefin particles are bound after the pattern of chains to form a porous layer on the outer surface side and very thin through holes are formed as extended from the inner surface side to the outer surface side. Though the microstructure of the hollow fiber membrane made of polypropylene is variable with the production conditions used for the hollow fiber membrane, it generally assumes the following pattern where, as the cooling and solidifying liquid, there is used a solution which shows no compatibility with an organic filler and possesses a specific heat capacity in the range of 0.3 to 0.7 cal/g. Specifically on the inner surface side, the solid phase has polypropylene particles partly exposed from the surface and preponderantly fused and bound intimately, namely fused and then cooled and solidified to give rise to a continuous phase.

Detailed Description Text (14):
The gaps intervening between such solid phases, in the wall thickness of the hollow fiber inclusively of the inner surface and the outer surface, form long paths extending from the inner surface to the outer surface. These pores are not extended linearly but continued reticularly in a complicated pattern to give rise to a three-dimensional network of through holes. This complexity of the through holes in distribution is evinced by the fact that the porous hollow fiber membrane of this invention possesses an extremely low birefringence ratio in the range of 0.001 to 0.01 in the axial direction of fiber and a small orientation of polypropylene crystals.

Detailed Description Text (15):
In the porous hollow fiber membrane of the present invention, the inner surface assumes desirable quality including smoothness because it comprises polypropylene particles which are partially exposed from the surface and proponderantly fused and bound closely to form a continuous phase and void portions which occupy the remaining matrix as described above. When this porous hollow fiber membrane is used in an oxygenator in such a manner as to pass blood through the inner cavity thereof, it neither inflicts any damage to the blood cell components nor aggravates

pressure loss. The outer surface thereof similarly assumes desirable surface quality inclusive of smoothness because it comprises a solid phase of a multiplicity of polypropylene clusters each composed of polypropylene particles orderly arranged in the axial direction of fiber and void portion occupying the remaining matrix.

Detailed Description Text (16):
When the porous hollow fiber membrane is used in an oxygenator in such a manner as to pass blood outside the hollow fiber, it neither inflicts any damage to the blood cell components nor aggravates pressure loss. Further, the pores of the porous hollow fiber membrane which serve as routes for passage of gas while the membrane is used in the oxygenator are formed of a three-dimensional network of through holes connected reticularly in a complicated pattern. No matter whether the blood for extracorporeal circulation is passed inside or outside the hollow fiber membrane, the blood plasma component is not allowed to pass through the long complicated rough routes offered by the pores. For instance, in the case of the extracorporeal circulation for 30 hours, it is observed neither occurrence of blood plasma leakage nor substantially decreasing the gas-exchange capacity.

Detailed Description Text (17):
Further, the porous hollow fiber membrane of this invention is, as described below, effected to thermal crimping, after offering it porosity by means of extracting, to obtain a crimped porous hollow fiber membrane treated with crimping without changing any features as described above, which membrane possesses an average crimp amplitude in the range of 35 to 120%, preferably 50 to 100%, of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, preferably 0.02 to 0.05, and a crimp ratio in the range of 1.0 to 3.0%, preferably 2.0 to 3.0%.

Detailed Description Text (18):
The treatment with crimping as described above has following advantage. For example, when an oxygenator which is formed of such porous hollow fiber as treated above is operated by circulating blood outside the hollow fiber membrane, while blowing an oxygen-containing gas inside the hollow fiber in the oxygenator, since gaps between the hollow fibers are relatively large and varied within a prescribed range over front and rear sides thereof in spite of the hollow fiber being hydrophobic, the air or oxygen-containing gas is hardly suffered to stagnate in the gaps. Thus, the hollow fiber membrane ensures satisfactory flow of blood and uniform contact of the blood with the oxygen-containing gas throughout the entire surface of the hollow fiber membrane. The hollow fiber membrane, therefore, manifests the gas-exchange capacity very efficiently.

Detailed Description Text (19):
The method for the production of a porous hollow fiber membrane contemplated by this invention is characterized by mixing a polyolefin, an organic filler uniformly dispersible in the polyolefin in the molten state thereof and easily soluble in a liquid extractant to be used, and a crystal seed forming agent, melting the resultant mixture and discharging the molten mixture through an annular spinning nozzle, allowing the discharged hollow thread to contact a cooling and solidifying liquid thereby cooling and solidifying the hollow thread, bringing the cooled and solidified hollow thread into contact with the liquid extractant incapable of dissolving the polyolefin thereby extracting the organic filler from the hollow thread, and thermally crimping the resultant hollow fiber membrane thereby forming a porous hollow fiber membrane possessing an average crimp amplitude in the range of 35 to 120% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, and a crimp ratio in the range of 1.0 to 3.0%.

Detailed Description Text (20):
The porous hollow fiber membrane of polyolefin which is obtained by causing the

organic filler incorporated in the molten dope as the raw material to be cooled and solidified and subsequently extracted therefrom with the liquid extractant as described above acquires a texture such that, as disclosed in Japanese Patent Laid-Open SHO 61(1986)-90,705, the inner surface side thereof has very small polyolefin particles closely bound to form a tightly packed layer and the outer surface side thereof has very small polyolefin particles connected after the pattern of chains to form a porous layer, with very thin through holes formed as extended from the inner surface side to the outer surface side. Since the pores are so minute and so complicated in distribution that the porous hollow fiber membrane acquires high permeability to gas and, at the same time, refrains from inducing the problem of blood plasma leakage.

Detailed Description Text (21):
When the porous hollow fiber membrane of this texture is vested with crimps of a prescribed ratio as described above and the oxygenator produced by incorporating therein the porous hollow fiber membrane is operating by circulating blood outside the hollow fiber membrane and blowing an oxygen-containing gas inside the hollow fiber membrane, the oxygen-containing gas such as air is hardly suffered to stagnate in the gaps and the blood is passed very smoothly and the blood and the oxygen-containing gas are brought into uniform contact throughout the entire surface of the hollow fiber membrane because the crimps of the description given above serve the purpose of interposing relatively large gaps between the adjacent hollow fibers and imparting alterations within a stated range to the hollow fibers throughout the whole length thereof. Thus, the porous hollow fiber membrane enjoys a very satisfactory gas-exchange capacity.

Detailed Description Text (23):
FIG. 1 is a schematic diagram illustrating a method for the production of a porous hollow fiber membrane of the present invention. In the embodiment illustrated in FIG. 1, a mixture 11 comprising a polyolefin, an organic filler, and a crystal seed forming agent is fed through a hopper 12 to a kneader such as, for example, a single-screw extruder 13, there to be melted and kneaded and extruded. The extruded mixture is forwarded to a spinning device 14 and discharged through an annular spinning nozzle (not shown) of a spinneret 15 into a gaseous atmosphere such as, for example, air.

Detailed Description Text (26):
While the hollow thread 16 is being conveyed on the belt conveyor 26 in the extruding machine 27, it is brought into ample contact with the liquid extractant 25 and deprived of the residual organic filler through extraction and consequently transformed into a hollow fiber membrane 16. The hollow fiber membrane 16' led out of the extruding machine 27 by drive rolls 22b is optionally passed through the steps of re-extraction and drying (not shown) and then guided by drive rolls 22c to a winding device 28 and, in this winding device 28, cross wound on a bobbin 29. Further, the hollow fiber membrane 16' taken up on the bobbin 29 is subjected to a heat treatment under suitable conditions to be set in a crimped state.

Detailed Description Text (29):
The mixing ratio of the polypropylene to the organic filler is desired to be such that the amount of the organic filler is in the range of 35 to 170 parts by weight, preferably 80 to 150 parts by weight, based on 100 parts by weight of the polypropylene. If the amount of the organic filler is less than 35 parts by weight, the produced porous hollow fiber membrane possesses no ample permeability to gas. Conversely, if the amount exceeds 170 parts by weight, the produced mixture possesses too low viscosity to be efficiently molded into a hollow thread.

Detailed Description Text (31):
The crystal seed forming agent to be in the raw material for this invention is an organic heat-resistant substance possessing a melting point exceeding 150.degree. C. (preferably falling in the range of 200.degree. to 250.degree. C.) and a gelling

point exceeding the crystallization initiating point of the polyolefin to be used. The crystal seed forming agent is incorporated for the sake of diminishing the polyolefin particles in size, reducing the gaps between the adjacent particles namely the through holes in thickness, and heightening the pore density. The crystal seed forming agents available herein include 1,3,2,4-dibenzylidene sorbitol, 1,3,2,4-bis(p-methylbenzylidine) sorbitol, 1,3,2,4,-bis(p-ethylbenzylidene)-sorbitol, bis(4-t-butylpheny) sodium benzoate, adipic acid, talc, and kaolin, for example.

Detailed Description Text (34):
The mixture prepared as the raw material as described above is further melted and kneaded by the use of an extruder such as, for example, a single screw extruder, at a temperature in the range of 160.degree. to 250.degree., preferably 180.degree. to 220.degree. C. and discharged, optionally by use of a gear pump of high metering accuracy, into the gaseous atmosphere through the annular nozzle of the spinning device to give rise to a hollow thread. The central part inside the annular nozzle may be caused to inhale spontaneously such a gas as nitrogen, carbon dioxide gas, helium, argon, or air or to introduce the gas forcibly. Then, the hollow thread discharged through the annular nozzle is let fall and subsequently brought into contact with the cooling and solidifying liquid in the cooling tank. The distance of this descent of the hollow thread is desired to be in the range of 5 to 1,000 mm, preferably 10 to 500 mm. This range is critical. If the distance of fall is less than 5 mm, the falling hollow thread is pulsated and possibly crushed at the moment of the entry thereof in the cooling and solidifying liquid. Inside the cooling tank, the hollow thread has not yet been thoroughly solidified and is susceptible of deformation under the external force because it contains a gas in the cavity thereof. The hollow thread 16 can be forcibly moved and, at the same time, prevented from being deformed under the external force (such as the pressure of fluid) by allowing the cooling and solidifying liquid 17 to flow down the interior of the cooling and solidifying liquid passing tube 19 disposed as thrust downwardly through the bottom of the cooling tank 18 and allowing the hollow' thread 16 to come into parallel contact with the downward flow of the cooling and solidifying liquid, for example, as illustrated in FIG. 1. As regard the flow rate of the cooling and solidifying liquid in this case, that which is attained by spontaneous flow is sufficient. At this time, the cooling temperature is desired to be in the range of 10.degree. to 90.degree. C., preferably 20.degree. to 75.degree. C. If this cooling temperature is lower than 10.degree. C., the cooling and solidifying proceeds so fast that the greater part of the wall of hollow fiber forms a tightly packed layer and the porous hollow fiber suffers from deficiency in gas-exchange capacity. Conversely, if this temperature exceeds 90.degree. C., the speed of crystallization of the polyolefin is so slow that the very thin through holes grow in diameter and the tightly packed layer grow very thin. This tightly packed layer is not formed at all when the temperature is higher. If the porous hollow fiber membrane of this quality is used in the oxygenator, it has the possibility of entailing either clogging or blood plasma leakage.

Detailed Description Text (38):
When the hollow thread in this state is completely cooled and solidified, the content of the organic filler in the hollow thread is low near the inner surface. After the organic filler is completely dissolved and extracted, the opening ratio is unduly low on the inner surface. Thus, the finally produced porous hollow fiber membrane is suspected to suffer from deficiency in gas-exchange capacity. In this particular case, the disadvantage may possibly ensue that even the low molecular component of the polypropylene is extracted from the hollow thread and accumulated on the inner wall of the cooling and solidifying liquid passing tube 19 to such an extent that the cooling and solidifying liquid passing tube 19 will have no sufficiently large inside diameter and the hollow thread will be disfigured.

Detailed Description Text (39):
If the cooling and solidifying liquid happens to be a compound identical or similar

to the organic filler, such as when a liquid paraffin is used as the cooling and solidifying liquid where a liquid paraffin having a number average molecular weight similar to that of the liquid paraffin used as the cooling and solidifying liquid is used as the organic filler, since the organic filler (liquid paraffin) is not appreciably migrated in the hollow thread, the hollow thread acquires a pore density as prescribed and not unduly large specific heat and, therefore, accelerates the crystallization of polypropylene at a proper cooling speed and assumes a stable shape. During the course of the cooling, however, the organic filler or the cooling and solidifying liquid is locally distributed in the outermost surface of the hollow thread before the hollow thread is thoroughly cooled and solidified, with the result that the polypropylene content of the hollow thread is low in the outermost surface and the pores in the outer surface of the hollow thread are large and the solid phase has polypropylene particles dispersed in the form of a network so as to give rise to a surface abundant with sharp rises and falls.

Detailed Description Text (40):
If the cooling and solidifying liquid happens to be a liquid incompatible with and inactive to the organic filler and yet ample in specific heat capacity, such as when water, a substance having such a large specific heat capacity of about 1.0 cal/g, is used where a liquid paraffin is used as the organic filler, there arises the possibility that, owing to the high cooling effect to be brought about consequently, the polypropylene is quickly cooled and the outer surface is suffered to assume a state of particularly low crystallinity. The possibility ensues, therefore, that the propylene fails to form very small particles and the hollow thread gives rise to a hollow fiber membrane containing unduly small pores in the outer surface and consequently exhibiting a low gas-exchange capacity. Conversely, if the cooling and solidifying liquid happens to have a small specific heat capacity, the cooling effect is not enough for the hollow thread to be completed as a hollow yarn.

Detailed Description Text (41):
When a solution showing no compatibility with the organic filler and possessing a specific heat capacity in the range of 0.3 to 0.7 cal/g is used as the cooling and solidifying liquid, the otherwise possible localization of the distribution of the organic filler in the outer surface of the hollow thread is precluded, the cooling of the polypropylene is allowed to proceed at a proper speed, and the crystallization of the polypropylene is accelerated without adversely affecting the proper polypropylene distribution ratio in the outer surface. As a result, the outer surface of the produced hollow fiber membrane, similarly to the interior thereof, is formed of an aggregate of a multiplicity of polypropylene clusters produced by very small polypropylene particles being bound in the axial direction of fiber and is allowed to assume a smooth surface.

Detailed Description Text (43):
For the liquid extractant to fulfil the purpose thereof, it has only to be incapable of dissolving the polypropylene forming the hollow fiber membrane and capable of dissolving and extracting the organic filler. Examples of the liquid extractant answering the description include alcohols such as methanol, ethanol, propanols, butanols pentanols, hexanols, octanols, and lauryl alcohol and halogenated hydrocarbons such as 1,1,2-trichloro-1,2,2,-trifluoroethane, trichlorofluoromethane, dichlorofluoromethane, and 1,1,2,2-tetrachloro-1,2,-difluoroethane. Among other liquid extractants mentioned above, hydrogenated hydrocarbons are particularly advantageous in terms of ability to effect the extraction of the organic filler and chlorofluorohydrocarbons are especially advantageous in terms of safety for the human body.

Detailed Description Text (44):
The porous hollow fiber membrane which is obtained as described above is subjected to a thermal crimping treatment. The thermal crimping treatment is aimed solely at

imparting crimps to the porous hollow fiber membrane in the prescribed ratio previously mentioned. The method which comprises cross winding the porous hollow fiber membrane on a bobbin, for example, and thermally setting it as wound on the bobbin as illustrated in FIG. 1 is not the only means available for the thermal crimping treatment. Alternatively, this treatment may be effectively accomplished by a method which comprises heating the porous hollow fiber membrane and passing the hot membrane between a pair of grooved rollers which are mutually meshed after the pattern of cogwheels or a method which comprises heating the porous hollow fiber membrane, forcing the hot membrane as folded in a zigzag pattern into a funnel-shaped hole, and pushing it out of the hole, for example.

Detailed Description Text (45):
In the method for the production of the porous hollow fiber membrane, since the porous hollow fiber membrane is made of a thermoplastic resin, the crimps in the prescribed ratio can be imparted thereto by preparatorily heating the porous hollow fiber membrane in a crimped state and allowing it cool thereby setting it in the crimped state. If the thermal treatment performed for the impartation of such crimps to an undue extent, the excess heat disfigures the membrane texture. If this disfigurement lowers the void ratio of the porous hollow fiber membrane even by more than 50% from the original value existing before the impartation of crimps, the porous hollow fiber membrane is no longer capable of manifesting the effect thereof fully. If the thermal treatment is insufficient, the porous hollow fiber membrane which retains a desired crimped state during the module assembly is eventually deprived of crimps under the tension exerted by the residual stress. Again in this case, the porous hollow fiber member fails to manifest the effect fully. In the method which comprises cross winding the porous hollow fiber membrane on a bobbin and heat setting it as wound on the bobbin as illustrated in FIG. 1, therefore, the heat setting is desired to be carried out at a temperature in the range of 50.degree. to 100.degree. C., preferably 60.degree. to 80.degree. C., for a period in the range of 2 to 48 hours, preferably 6 to 36 hours.

Detailed Description Text (46):
The porous hollow fiber membrane obtained as described above is used optimally in the hollow fiber type oxygenator.

Detailed Description Text (47):
The hollow fiber membrane obtained by the conventional stretching method possess too high permeability to as to be efficiently in the oxygenator. When the blood is circulated inside the hollow fiber the ability to add oxygen to the blood is affected by the fact that the resistance offered by the membrane on the side bordering on the blood is unduly large and the resistance offered by the hollow fiber membrane lacks constancy and the ability to remove carbon dioxide gas from the blood depends on the magnitude of the resistance offered by the hollow fiber membrane which possesses unduly high permeability to gas. When the blood is circulated outside the hollow fiber, the ability to effect exchange of gases depends on the magnitude of the resistance offered by the hollow fiber membrane which again manifests unduly high permeability to gas.

Detailed Description Text (48):
The hollow fiber membrane of this invention itself possesses lower permeability to gas than the countertype obtained by the conventional stretching method. It fulfils the performance fully when it is used as incorporated in the oxygenator. Since it is produced by the extraction method, it cannot form pinholes susceptible of leakage of blood and, therefore, can be prevented from degradation of gas-exchange capacity.

Detailed Description Text (49):
Further, the hollow fiber membrane which is obtained by using, as the cooling and solidifying liquid, a liquid identical or similar to the organic filler has very small polypropylene particles connected after the pattern of a network so as to

give rise to a surface abundant with very sharp rises and falls as previously mentioned. When this hollow fiber membrane is incorporated in the oxygenator, therefore, there arises the possibility that the adjacent hollow fibers coalesce fast to such an extent that the work of assembly is complicated and the adhesive agent is obstructed from amply enveloping the individual hollow fibers and giving rise to a desirable potting.

Detailed Description Text (50):
In the case of the hollow fiber membrane obtained by the method of the present invention, such drawbacks as involved in the assembly of the oxygenator cannot occur because the outer surface thereof, similarly to the interior thereof, is formed of an aggregate of a multiplicity of polypropylene clusters composed of polypropylene particles connected in the axial direction of fiber and, therefore, is allowed to acquire satisfactory surface quality inclusive of smoothness. No matter whether the blood may be passed on the outer surface or the inner surface of the hollow fiber membrane, this hollow fiber membrane inflicts no damage on the blood cell components and suffers from apparent pressure loss.

Detailed Description Text (51):
Further, since the hollow fiber membrane obtained by the method of this invention contains crimps at a prescribed ratio as previously mentioned, the gaps between the adjacent hollow fibers are relatively large and are varied within a limited range throughout the entire length of fiber. Even when the blood is circulated outside the hollow fiber membrane and the oxygen-containing gas is blown inside the hollow fiber membrane, the stagnation of the oxygen-containing gas such as air can hardly occur in these gaps. The hollow fiber membrane, therefore, ensures smooth flow of the blood and permits uniform contact between the blood and the oxygen-containing gas throughout the entire surface of the hollow fiber membrane and manifests a satisfactory gas-exchange capacity fully.

Detailed Description Text (52):
FIG. 2 illustrates a typical hollow fiber membrane type oxygenator as one embodiment (first embodiment) of this invention, specifically assembled for circulating blood inside the hollow fiber membrane and blowing the oxygen-containing gas outside the hollow fiber membrane. The hollow fiber membrane type oxygenator 51 is furnished with a housing 52. This housing 52 is provided at the opposite ends of a tubular main body 53 respectively with annular male-thread fitting covers 54, 55. Inside the housing 52, a multiplicity in the range of 10,000 to 60,000, for example, of porous hollow fiber membranes 16' crimped at a prescribed ratio previously mentioned are parallelly disposed in the longitudinal direction of the housing 52 as mutually separated. The opposite end parts of the porous hollow fiber membranes 16' are watertightly supported inside the fitting covers 54, 55 by diaphragms 57, 58 in such a manner that the openings thereof are not closed. The diaphragms 57, 58 define and enclose a gas compartment 59 jointly with the outer surfaces of the porous hollow fiber membranes 16' and the inner surface of the housing 52 and, at the same time, isolate the gas compartment 59 from the blood passing cavities (not shown) formed inside the porous hollow fiber membranes 16'. The fitting cover 54 is provided with an oxygen-containing gas inlet 60 for supply of an oxygen-containing gas and the other fitting cover 55 with an oxygen-containing gas outlet 16 for discharge of the oxygen-containing gas.

Detailed Description Text (53):
The tubular main body 53 of the housing 52 may be provided on the inner surface thereof at the center in the axial direction with an inwardly projected constringent part 62. The constringent part 62 disposed in the central part can be expected to improve the gas-exchange efficiency. This high gas-exchange efficiency can be obtained without requiring the provision of this constringent part 62, however, because the porous hollow fiber membranes 16' used in the oxygenator of the present invention are crimped at the prescribed ratio as already mentioned. The constringent part 62 is formed on the inner surface of the tubular main body 53

integrally with the tubular main body 53 and adapted to constrict the overall circumference of a hollow fiber bundle 63 composed of the multiplicity of porous hollow fiber membranes 16' inserted inside the tubular main body 53. Thus, the hollow fiber bundle 63 is constricted at the center in the axial direction thereof to give rise to a constricted part 64. The packing ratio of hollow fiber membranes, therefore, varies along the axial direction of the constricted part 64 and reaches the maximum at the center. The packing ratios at different parts are desired to be selected as follows. The packing ratio A in the constricted part 64 at the center is approximately in the range of 60 to 80%, the packing ratio B in the interior of the tubular main body 53 approximately in the range of 30 to 60%, and the packing ratio C at the opposite ends of the hollow fiber bundle 63, namely on the outer surfaces of the diaphragms 57, 58, approximately in the range of 20 to 40%.

Detailed Description Text (54):
Now, the formation of the diaphragms 57, 58 will be described below. As described above, the diaphragms 57, 58 fulfil an important function of isolating the inner cavities of the porous hollow fiber membranes 16' from the outside. Generally, the diaphragms 57 are produced by casting a macromolecular potting material of high polarity such as, for example, polyurethane, silicone, or epoxy resin on the opposite inner walls of the housing 52 by the centrifugal casting method and allowing the deposited layers of the potting material to set. To be more specific, a multiplicity of porous hollow fiber membranes 16' of a length greater than the length of the housing 52 are prepared and, with the opposite open ends thereof filled with a highly viscous resin, are arranged in place inside the tubular main body 53 of the housing 52. Then, with the opposite ends of the porous hollow fiber membranes 16' completely covered each with a pattern cover larger than the diameter of the fitting covers 54, 55, the housing 52 is rotated around the central axis of the housing 52 and, at the same time, the macromolecular potting material is cast from the opposite end sides. When the cast resin is set, the pattern covers are removed and the outer lateral parts of the set layers of resin are cut off with a sharp blade and the opposite open ends of the porous hollow fiber membranes 16' are exposed. As a result, the diaphragms 57, 58 are formed.

Detailed Description Text (56):
FIG. 4 illustrates another typical hollow fiber membrane type oxygenator as another embodiment (second embodiment) of this invention, specifically assembled so as to circulate blood outside the hollow fiber membrane and blow an oxygen-containing gas inside the hollow fiber. The hollow fiber membrane type oxygenator 81 is furnished with a housing 82. This housing 82 is provided at the opposite end parts of a tubular main body 83 thereof respectively with annular fitting covers 84, 85. Inside the housing 82, a multiplicity in the range of 10,000 to 70,000, for example, of porous hollow fiber membranes 16' possessing the properties mentioned previously are parallelly arranged in the longitudinal direction of the housing as mutually separated. The opposite end parts of the porous hollow fiber membranes 16' are watertightly supported in place respectively inside the fitting covers 84, 85 by diaphragms 87, 88 in such a manner that the openings thereof are not closed. The diaphragms 87, 88 form and enclose a blood compartment 89 jointly with the peripheral surface of the porous hollow fiber membranes 16' and the inner surface of the housing 82 and isolate oxygen-containing gas flowing cavities (not shown) formed inside the porous hollow fiber membranes 16' from the blood compartment 89. The housing 82 is provided in one part thereof with a blood inlet 95 for supply of blood and in the other part thereof with a blood outlet 96 for discharge of blood.

Detailed Description Text (57):
The tubular main body 83 of the housing 82 may be provided on the inner surface thereof at the center in the axial direction with a projecting constringent part 92. The constringent part 92 integrally with the tubular main body 83 and adapted to constrict the overall periphery of a hollow fiber bundle 93 composed of a multiplicity of porous hollow fiber membranes 16' inserted in the interior of the tubular main body 83. Thus, the hollow fiber bundle 93 is constricted at the center

in the axial direction thereof to form a constricted part 94. The packing ratio of hollow fiber membranes, therefore, varies in the axial direction of fiber and reaches the maximum at the center. In the fitting covers 84, 85, an oxygen-containing gas inlet 90 and an oxygen-containing gas outlet 91 are respectively formed. The other components and the method for the formation thereof are equivalent, with due modifications, to those of the hollow fiber membrane type oxygenator of the first embodiment. Thus, the description thereof will be omitted.

Detailed Description Text (60):
A porous hollow fiber membrane of polypropylene formed by being stretched in the axial direction by the stretching method, having an inside diameter of 200 .mu.m and a wall thickness of 24 .mu.m and containing very small pores having an average radius of 700.ANG. was cross wound on a bobbin 95 mm in diameter and then crimped by heat treating at 60.degree. C. for 18 hours. The porous hollow fiber membrane obtained consequently had an average crimp amplitude of 70% of the outside diameter of the hollow fiber membrane, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio of 0.03, and a crimp ratio of 2.5%. From this crimped porous hollow fiber membrane, an oxygenator of the first embodiment, an oxygenator of the second embodiment, and an oxygenator conforming to the first embodiment, except that the hollow fiber bundle was not constricted at the center in the axial direction, (third embodiment) were produced as respective module in the manner described below. They were tested for oxygen gas flux, ability to add oxygen gas, and ability to remove carbon dioxide gas. The results are shown in Table 3.

Detailed Description Text (62):
For comparison, the same oxygenator modules as those of Example 1 were produced by using without any modification a porous hollow fiber membrane of polypropylene formed by being stretched in the axial direction by the stretching method, having an inside diameter of 200 .mu.m and a wall thickness of 24 .mu.m, and containing very small pores having an average radius of 700.ANG.; the module of the first embodiment for Control 1 and that of the second embodiment for Control 2 respectively. These oxygenator modules were tested for oxygen gas flux, ability to add oxygen gas, and ability to remove carbon dioxide gas. The results are shown in Table 3.

Detailed Description Text (65):
The properties were determined by randomly drawing 10 of the hollow fiber membranes of a given oxygenator cutting them into tubes about 0.5 in length with a sharp razor blade, projecting the sections of the tubes on a screen with a universal projector (Nikon Profile Projector V-12), measuring the outside diameters d.sub.1 and inside diameters d.sub.2 of the projected sections with a counter (Nikon Digital counter CM-6S), and calculating the wall thickness t by the formula t=d.sub.1 -d.sub.2. The respective averages each of 10 measured values were reported.

Detailed Description Text (67):
This property was determined by taking about 2 g of the hollow fiber membranes of a given oxygenator, cutting them into tubes not more than 5 mm in length with a sharp razor, pressing the resultant test specimen to a pressure of 1,000 kg/cm.sup.2 with a mercury porosimeter (Carlo Erba Corp; Motem 65A), finding the total volume of pores (volume of pores in the hollow fiber per unit weight), and calculating the void ratio.

Detailed Description Text (69):
A given hollow fiber membrane was tested for crimped condition by the measurement of rises and falls on the membranes surface over a length of 35 mm with a universal surface shape tester (produced by Kosaka Kenkyusho K. K. and marketed under product code of "SE-3S") to determined the largest (A) of amplitudes found in round of measurement and the ratio (A/B) of this maximum amplitude (A) to the distance (B) between the maximum point and the minimum point in the amplitude. Ten rounds of the

measurement were made per lot and the average of the ten found values was reported as the maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio. The average of ten largest of the amplitudes found in one round of measurement was reported as the average crimp amplitude.

Detailed Description Text (71):
This property was determined by subjecting a given hollow fiber membrane in an initial length of 25 mm to a tensile test with a tensile tester (produced by Toyo Seiki K. K. and marketed under trademark designation of "Strograph T") thereby finding the lengths of the sample acquired under two loads, 1 mg and 50 mg per denier, and dividing the difference of the two distances by the initial length. The results quotient in percentage was reported as the magnitude of this property.

Detailed Description Text (73):
This property was determined by preparing a miniature module 14 cm in available length and 0.025 m.sup.2 in available membrane area with a given porous hollow fiber membrane, closing one end of the miniature module, exerting one atmosphere of pressure on the interior of the hollow membrane with oxygen until a steady state was obtained, and measuring the flow volume of oxygen gas with a flow meter (produced by Kusano Rikagakukiki Seisakusho and marketed under trademark designation of "Flotomer"). The scale reading was reported as the magnitude of this property.

Detailed Description Text (76):
These properties were determined by preparing an oxygenator module 130 mm in available length and 5.4 m.sup.2 in available membrane area using a given hollow fiber membrane, passing bovine blood (standard venous blood) in a single path inside the hollow fiber membrane at a flow volume of 6.0 lit/min., passing purified oxygen outside the hollow fiber membrane at a flow volume of 6.0 lit/min. measuring the pH, partial pressure of carbon dioxide gas (PCO.sub.2), and partial pressure of oxygen gas (PO.sub.2) of the bovine blood samples taken at the inlet and outlet of the oxygenator with a blood gas measuring device (produced by Radiometer Corp. and marketed under product code of "BGA 3" and calculating the differences of partial pressure at the inlet and outlet of the oxygenator. The detailed specification of the oxygenator, module is shown in Table 1. The quality of the standard venous blood is shown in Table 2.

Detailed Description Text (78):
The properties were determined by preparing an oxygenator module 90 mm in available length and 2.1 m.sup.2 in available membrane area using a given hollow fiber membrane, passing bovine blood (standard venous blood) in a single path outside the hollow fiber membrane at a flow volume of 6.0 lit/min., passing purified oxygen inside the hollow fiber membrane at a flow rate of 6.0 lit/min, measuring the pH value, partial pressure of oxygen inside the hollow fiber membrane at a flow rate of 6.0 min, measuring the pH value, partial pressure of carbon dioxide gas (PCO.sub.2), and partial pressure of oxygen gas (PO.sub.2) of the bovine blood samples taken at the inlet and outlet of the oxygenator with a blood gas measuring device (produced by Radiometer Corp. and marketed under product code of "BGA3"), and calculating the difference of partial pressures at the inlet and outlet of the oxygenator. The detailed specification of the oxygenator module is shown in Table 1.

Detailed Description Text (82):
By use of a twin-screw extruder (produced by Ikegai Iron Works, Ltd. and marketed under produce code of "PCM-30-25"), 100 parts by weight of a propylene homopolymer having a melt index (M.I.) of 23, 130 parts by weight of a liquid paraffin (number average molecular weight 324), and 0.5 part by weight of 1,3,2,4-bis(ethylbenzene) sorbitol as a crystal seed forming agent were melted and kneaded and extruded and then pelletized. By use of a device illustrated in FIG. 2, namely a single-screw extruder (produced by Kasamatsu Seisakusho and marketed under product code of "WO-

30"), the pellets were melted at 180.degree. C. and discharged into the ambient air at a rate of 3.6 to 5.0 g/min through an annular spinning nozzle 4 mm in core diameter, 6 mm in inside diameter, 7 mm in outside diameter, and 15 mm in land length to let fall a hollow thread 16. The distance of this fall was 20 to 30 mm. Then, the hollow thread 16 was brought into contact with Freon 113 (1,1,2-trichloro-1,2,2,-trifluoroethylene) held as a cooling and solidifying liquid 17 in a cooling tank 18, and then cooled by being brought into parallel contact with a cooling and solidifying liquid 17 spontaneously falling down the interior of a cooling and solidifying liquid passing tube 19. In this case, the temperature of the cooling and solidifying liquid 17 was 20.degree. C. Then, the hollow thread 16 was introduced into the cooling and solidifying liquid 17 held in a solidifying tank 20, caused to change the direction of its travel by a direction changing bar 21, led to a drive roll 22a operated at a winding speed of 80 m/min and, immediately in a shower conveyor type extruder 27, showered with a liquid extractant 25 using Freon 113 for thorough extraction of the aforementioned liquid paraffin. The hollow fiber membrane 16' which had been vested with porosity as described above was taken out of the extruder 27 by means of drive rolls 22b, forwarded via drive rolls 22c to a winder 28, and taken up by cross winding on a bobbin 29 having a diameter of 95 mm by means of the winder 28. The hollow fiber membrane 16' thus taken up in cross winding on the bobbin 29 was crimped by being heat treated in an oven at 60.degree. C. for 18 hours.

Detailed Description Text (83):
The porous hollow fiber membrane consequently obtained was found to possess an average crimp amplitude of 72% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio of 0.03, and a crimp ratio of 1.7%. From the crimped porous hollow fiber membrane, an oxygenator of the first embodiment, an oxygenator of the second embodiment, and an oxygenator module (third embodiment) identical to that of the first embodiment, except that the hollow fiber bundle was not constricted at the center in the axial direction, were prepared. The oxygenator modules were tested for oxygen gas flux, ability to add oxygen gas, ability to remove carbon dioxide gas, and blood plasma leakage. The results are shown in Table 5. Table 4 shows the conditions for the embodiments mentioned above.

Detailed Description Text (85):
A porous hollow fiber membrane was prepared by following the procedure of Example 4, except that the crimping treatment was omitted. From this porous hollow fiber membrane, modules of an oxygenator of the first embodiment and an oxygenator of the second embodiment were prepared. These modules were tested for oxygen gas flux, ability to add oxygen gas, ability to remove carbon dioxide gas, and blood plasma leakage. The results are shown in Table 5.

Detailed Description Text (87):
A porous hollow fiber membrane of polypropylene formed by being stretched in the axial direction by the stretching method, having an inside diameter of 200 .mu.m and a wall thickness of 25 .mu.m and containing very small pores 700.ANG. in average radius was taken up in cross winding on a bobbin 95 mm in diameter and crimped by being heat treated in an oven at 60.degree. C. for 18 hours. The porous hollow fiber membrane thus obtained was found to have an average crimp amplitude of 70% of the outside diameter of hollow fiber membrane, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio of 0.03, and a crimp ratio of 2.5%. From this porous hollow fiber membrane, an oxygenator of the first embodiment, an oxygenator of the second embodiment, and an oxygenator of the third embodiment were produced. These oxygenator modules were tested for oxygen gas flux, ability to add oxygen gas, ability to remove carbon dioxide gas, and blood plasma leakage. The results are shown in Table 5.

Detailed Description Text (89):
A porous hollow fiber membrane was obtained by following the procedure of Example

4, except that polyethylene glycol (Mn=200) was used in place of Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethylene) as the cooling and solidifying liquid.

Detailed Description Text (90):
This porous hollow fiber membrane was found to have an average crimp amplitude of 72% of the outside diameter of the hollow fiber membrane, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio of 0.03, and a crimp ratio of 1.7%. The crimped porous hollow fiber membrane was tested for shape (inside diameter/wall thickness), void ratio, gas flux, and birefringence ratio as an index of crystal orientation. The results are shown in Table 6. From this crimped porous hollow fiber membrane, an oxygenator of the first embodiment, an oxygenator of the second embodiment, and an oxygenator module (third embodiment) identical to the oxygenator of the first embodiment, except that the hollow fiber bundle was not constricted at the center in the axial direction. These oxygenator modules were tested for ability to add oxygen gas, ability to remove carbon dioxide gas, and blood plasma leakage. The results are shown in Table 6.

Detailed Description Text (96):
From a batch of hollow fiber membranes, 10 membranes were randomly taken. From the central parts of these samples, portions 3 cm in length were cut off. By inserting oblique cuts at one end of these portions, test pieces were obtained.

Detailed Description Text (97):
These test pieces were placed on a slide glass, impregnated with a soaking liquid (liquid paraffin), and mounted on a rotary stage of a polarizing microscope. With the aid of a monochromic light source or a filter and with the compensator removed, the test pieces were rotated on the stage under cross Nicol prism and then fixed at the position at which the vision was brightest (the position reached by 45.degree. rotation from the darkest position). Then, the compensator was replaced and the analyzer was rotated to find the angle (.theta.) of rotation required in reaching the darkest position. The retardation (R) was calculated from the following formula and the birefringence ratio of the hollow fiber membrane was calculated from the following formula. The average of the value of 10 measurements was reported as the magnitude of birefringence factor. ##EQU1## wherein .lambda. is the wavelength used in the test. ##EQU2## wherein d is the thickness of test piece (corrected with respect to the void ratio).

Detailed Description Text (104):
Similar tests as in Example 4 were conducted by use of hollow fiber membranes obtained by repeating the procedure of Example 4 except that maximum crimp amplitude/crimp half cycle ratios and crimp amplitudes of the outside diameter were varied as shown in Table 7. The results are shown in Table 7.

Detailed Description Text (106):
Similar tests as in Example 5 were conducted by use of hollow fiber membranes obtained by repeating the procedure of Example 5 except that maximum crimp amplitude/crimp half cycle ratios and crimp amplitudes of the outside diameter were varied as shown in Table 8. The results are shown in Table 8.

Detailed Description Text (107):
As described above, this invention is directed to a porous hollow fiber membrane of polyolefin having an inside diameter in the range of 150 to 300 .mu.m and a wall thickness in the range of 10 to 150 .mu.m and a wall thickness in the range of 10 to 150 .mu.m and a substantially circular cross section, which porous hollow-fiber membrane is characterized by the fact that the inner surface side thereof has very small particles of the polyolefin closely bound to form a tightly packed layer, the inner surface side thereof has very small particles of the polyolefin bound after the pattern of chains to form a porous layer, very thin through holes are formed as extended from the inner surface side to the outer surface side, and the hollow fiber membrane has an average crimp amplitude in the range of 35 to 120% of the

outside diameter, a maximum crimp amplitude/crip half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, and a crimp ratio in the range of 1.0 to 3.0%.

Detailed Description Text (108):
When an oxygenator is produced by using the porous hollow fiber membrane and this oxygenator is operated for extracorporeal circulation by circulating blood outside the hollow fiber membrane and blowing an oxygen-gas containing gas inside the hollow fiber membrane, since the crimps give rise to relatively large gaps between the adjacent hollow fibers and the gaps are varied within a prescribed range throughout the entire length of hollow fiber, the oxygen-containing gas such as air is hardly suffered to stagnate in the gaps. As a result, the oxygenator enjoys a high gas-exchange capacity because the blood is passed smoothly and the blood and the oxygen-containing gas are brought into uniform mutual contact throughout the entire surface of the hollow fiber membrane. The oxygenator cannot entail the problem of blood plasma leakage, for example, on account of the texture of membrane. The effects of the porous hollow fiber membrane of this invention described above are manifested .mu.more advantageously when the porous hollow fiber membrane has a void ratio in the range of 5 to 60% and a gas flux in the range of 100 to 1,500 liters/min.m.sup.2. atm., the polyolefin is polypropylene, and the porous hollow fiber membrane has an average crimp amplitude in the range of 50 to 100% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.02 to 0.05, and a crimp ratio in the range of 2.0 to 3.0%. Thus, this porous hollow fiber membrane is used more advantageous for the oxygenator.

Detailed Description Text (109):
During the course of assembly an oxygenator using the porous hollow fiber membrane, since this porous hollow fiber membrane has satisfactory surface quality inclusive of smoothness, such drawbacks as coalescence of adjacent hollow fiber membranes and defective potting due to adhesive agent are not entailed. When the oxygenator using the porous hollow fiber membrane of such highly desirable quality is used for extracorporeal blood circulation by circuiting the blood outside the hollow fiber membrane in the oxygenator and blowing the oxygen-containing gas inside the hollow fiber membrane, since the crimps give rise to relatively large gaps between the adjacent hollow fibers and the gaps are varied within a prescribed range throughout the entire length of hollow fiber as described above, the oxygen-containing gas such as air is hardly suffered to stagnate in the gaps. As a result, the oxygenator enjoys a high gas-exchange capacity because the blood is passed smoothly and the blood and the oxygen-containing gas are brought into uniform mutual contact throughout the entire surface of the hollow fiber membrane. These features are manifested more advantageously when the birefringence ratio of the porous hollow fiber membrane in the axial direction of fiber is in the range of 0.001 to 0.01.

Detailed Description Text (110):
This invention is also directed to a method for the production of a porous hollow fiber membrane, which is characterized by mixing a polyolefin, an organic filler uniformly dispersible in the polyolefin in the molten state thereof and easily soluble in a liquid extractant to be used, and a crystal seed forming agent, melting the resultant mixture and discharging the molten mixture through annular spinning nozzles into hollow threads, allowing the hollow threads to contact a cooling and solidifying liquid incapable of dissolving the polyolefin thereby cooling and solidifying the hollow threads, then bringing the resultant cooled and solidified hollow threads into contact with the liquid extractant incapable of dissolving the polyolefin thereby extracting the organic filler from the hollow threads, and thermally crimping the hollow threads thereby forming porous follow fiber membranes possessing an average crimp amplitude in the range of 35 to 120% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.01 to 0.1, and a crimp ratio in the range of 1.0 to 3.0%.

Detailed Description Text (111):
By this method can be produced a porous hollow fiber membrane which possesses such outstanding properties as mentioned above, including an enhanced gas-liquid contact efficiency in the gas exchange and sacrificing none of the desirable microporous texture and gas-exchange efficiency of the porous hollow fiber membrane produced by the extraction method. In the method of the present invention for the production of a porous hollow fiber membrane, the produced porous hollow fiber possessing a shape abundant with gas-liquid contact efficiency, a texture notably excellent in other properties, and a stable behavior when the impartation of crimps is effected by cross winding the hollow fiber membrane on a bobbin and heat setting it as wound on the bobbin and this heat setting is carried out at a temperature in the range of 50.degree. to 100.degree. C. for a period in the range of 2 to 48 hours. Further, the produced hollow fiber membrane enjoys a still better quality when the polyolefin is polypropylene, the organic filler is a hydrocarbon having a boiling point exceeding the melting point of the polyolefin, the hydrocarbon is a liquid paraffin or an .alpha.-olefin oligomer, the amount of the organic filler to be incorporated is in the range of 35 to 170 parts by weight, based on 100 parts by weight of the polyolefin, the crystal seed forming agent is an organic heat-resistant substance having a melting point exceeding 150.degree. C. and a gelling point exceeding the crystallization initiating point of the polyolefin to be used, and the amount of the crystal led forming substance to be incorporated is in the range of 0.1 to 5 parts by weight, based on 100 parts by weight of the polyolefin.

Detailed Description Text (112):
This invention is further directed to an oxygenator provided with a hollow fiber membrane as a gas-exchange membrane, which oxygenator is characterized by the fact that the gas-exchange membrane is a porous hollow fiber membrane of a polyolefin having an inside diameter in the range of 150 to 300 and a wall thickness in the range of 10 to 150 .mu.m and a substantially circular cross section, the inner surface side thereof has very small particles of the polyolefin closely bound to form a tightly packed layer, the outer surface side thereof has very small particles of the polyolefin interconnected after the pattern of chains to form a porous layer, very thin through holes are formed as extended from the inner surface side to the outer surface side, and the porous hollow fiber membrane has an average crimp amplitude in the range of 35 to 120% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 1.0% to 3.0%. This oxygenator, therefore, does not suffer from such drawbacks as blood plasma leakage. When this oxygenator is used for extracorporeal circulation of blood by circulating the blood outside the hollow fiber membrane and an oxygen-containing gas inside the hollow fiber membrane, the possibility of the oxygen-containing gas stagnating in the gaps intervening between the adjacent hollow fibers is nil and the gas-exchange is carried out efficiently. When the oxygenator is used for extracorporeal blood circulating by circulating the blood inside the hollow fiber membrane and blowing the oxygen-containing gas outside the hollow fiber membrane, it is capable of carrying out the gas exchange with high efficiency. In this case, the highly efficient gas exchange can be obtained without requiring the hollow fiber bundle to be constricted at the center in the axial direction. In the oxygenator of the lung intended for passing the blood inside the hollow fiber membrane, since the steam contained in the oxygen-containing gas inside the oxygenator is condensed to form dew on the inner surface of the housing of the oxygenator, there arises the possibility of water drops wetting the surface of the hollow fiber and the wetted hollow fiber adhering fast to the inner surface of the housing. Thus, gaps of prescribed dimensional properties interposed between the hollow fiber bundle and the inner surface of the housing so as to keep the hollow fiber bundle from adhering fast to the inner surface of the housing. If a continuous gap is formed throughout the entire length of the hollow fiber bundle, the passage of gas occurs exclusively in the continuous gap. Thus the oxygenator is provided at the center in the axial direction with a constricted part which is intended to render the phenomenon of channeling difficult to occur. When the

crimped hollow fiber membrane contemplated by the present invention is used, since the hollow fiber membrane itself is crimped, the dew possibly formed on the inner surface of the housing cannot cause tight adhesion of the hollow fiber membrane to the inner surface of the housing even if no large space is interpose(between the hollow fiber membrane and the inner surface of the housing. Thus, the oxygenator is allowed to retain the gas-exchange efficiency intact even in the absence of the constricted part. The oxygenator of this invention is enabled to manifest the quality more advantageously and even permit a reduction in size when the hollow fiber membrane has a void ratio in the range of 5 to 60%, a gas flux in the range of 10 to 1,500 liters/min.m.sup.2 atm, the polyolefin is polypropylene, and the hollow fiber membrane has an average crimp amplitude in the range of 50 to 100% of the outside diameter, a maximum crimp amplitude/crimp half cycle period at maximum crimp amplitude ratio in the range of 0.02 to 0.05, and a crimp ratio in the range of 2.0 to 3.0%.

CLAIMS:

1. An oxygenator comprising:

a container having a blood inlet, a blood outlet, an oxygen-containing gas inlet and an oxygen-containing gas outlet; and

a plurality of hydrophobic porous hollow fiber membranes, housed within said container, for defining therein passages for an oxygen-containing gas between said oxygen-containing gas inlet and said oxygen-containing gas outlet, and for defining a passage for blood outside said fiber membranes between said blood inlet and said blood outlet, said fiber membranes having an inside diameter of 150 to 300 .mu.m, a wall thickness of 10 to 150 .mu.m, and a substantially circular cross-section, an average crimp amplitude of 50 to 120% of the outside diameter thereof, a ratio of the maximum crimp amplitude to a crimp half cycle period at the maximum crimp amplitude in the range of 0.01 to 0.1, and a crimp ratio of 1.0 to 3.0%.

8. An oxygenator according to claim 1, wherein said fiber membrane has on the inner wall side a tightly packed layer in which minute polyolefin particles are intimately bound, and on the outer wall side a porous layer in which minute polyolefin particles are bound in a chain-like pattern, so that fine through-pores are formed in said fiber membrane between the inner and outer surfaces thereof.

10. An oxygenator according to claim 1, wherein said fiber membrane has on the inner wall side thereof a continuous layer of densely fused polypropylene, said continuous layer having part of polypropylene particles being exposed, and on the outer wall side thereof and between the inner and outer wall sides a chained layer of a plurality of polypropylene chains extending in the axial direction of said fiber membrane, said fiber membrane containing fine pores which establish communication between the inner and outer sides in the form of a three-dimensional network.

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